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XCVIII. *Why Wireless Electric Rays can bend round the Earth.* *By* Sir JOSEPH LARMOR, *F.R.S.**

THE earliest announcement that electric signals through free æther had been successfully detected as far as America by the Marconi operators, gave rise to a prompt query from the late Lord Rayleigh as to how the rays could manage to bend round the protuberance of the curved earth. In fact, in a single medium propagating waves without absorption or dispersion, all features remain similar when the scales of space and time are altered in the same ratio: thus waves of length λ bending round the earth of radius a will behave similarly to waves of length $k\lambda$ bending round a smaller sphere of like quality of radius ka. To change from electric waves 10^4 cm. long to waves of light 10^{-4} cm. long, k would be 10^{-8}; hence the radius of the sphere corresponding to the earth would be $10^{-8} . 10^9/\frac{1}{2}\pi$ or 6 cm.; and familiar experience indicates that visible light could hardly creep to a sensible degree round one-tenth of the circumference of a sphere of that radius. To elucidate this subject quantitatively in those early days involved difficult and extensive calculations of the problem of diffraction of waves by a boundary, conducting or dielectric, of continuous curvature; and investigations by Lord Rayleigh, H. M. Macdonald, A. E. H. Love, J. W. Nicholson,

* Read at the Cambridge Philosophical Society, Oct. 27. Communicated by Sir Oliver Lodge.

G. N. Watson and others have widely extended that domain of mathematical optics.

But nowadays, when ray-signals are readily received at the antipodes, all shadow of uncertainty as to the facts is removed. The rays could not travel free, except in straight lines, in a medium of practically uniform speed of propagation such as ordinary air ; either they must be guided by being linked to the surface of the earth, much as cylindrical Hertzian waves follow a guiding central wire, or else the speed of propagation must for some cause increase notably upwards so as to bend them down. Very early observations by Admiral (then Captain) Jackson with the help of British cruising squadrons, showed that the high table-land of Spain was not an effective obstacle, which perhaps already pointed to transmission of the rays high in the atmosphere.

The ultra-rarefied upper atmosphere with its long free path must be subject to strong ionization by the incident ultra-violet solar radiation, the effect persisting after daytime, and appeal has been generally made to such a conducting layer to provide the necessary increase of velocity of the rays. But ordinary electric conduction operates by introducing a frictional term causing absorption into the equations, and it is a familiar principle that when the absorption is of the first order the change of speed is only of the second order, so that if the latter change is to be adequate, the rays would be damped out immediately instead of being sensibly transmitted. In rough illustration, the usual type (including the optical) of equation of propagation with frictional resistance of modulus κ

$$\frac{\partial^2\phi}{\partial t^2}+\kappa\frac{\partial\phi}{\partial t}=c^2\frac{\partial^2\phi}{\partial x^2}$$

is satisfied by

$$\phi=\mathrm{A}e^{-imx}e^{int},$$

where $n^2-\kappa ni=m^2c^2$, so that, for a real period $2\pi/n$,

$$mc=(n^2-i\kappa n)^{\frac{1}{2}}=n\left(1-\tfrac{1}{2}i\frac{\kappa}{n}+\frac{1}{8}\frac{\kappa^2}{n^2}+\ldots\right).$$

Thus, retaining real parts, we arrive at a simple wave-train of type

$$\phi=\mathrm{A}e^{-\frac{1}{2}\frac{\kappa}{c}x}\cos n\left\{t-\left(1+\frac{1}{8}\frac{\kappa^2}{n^2}\right)\frac{x}{c}\right\}$$

with extinction modulus $\frac{1}{2}\kappa/c$ and velocity of propagation

$$v=c\left(1+\frac{1}{8}\frac{\kappa^2}{n^2}\right)^{-1}, \text{ or say } c\left(1-\frac{1}{8}\frac{\kappa^2}{n^2}\right),$$

thus smaller than c, but only to the second order in κ.

(On the principle of ray-curvature as *infra*, a ray of assigned period will adapt itself to the curvature of the earth only when

$$\tfrac{1}{2}\pi\, 10^{-9}=\frac{d}{dh}\log v=-\frac{1}{8n^2}\frac{d}{dh}\kappa^2.$$

The attenuation would vary inversely as the wave-length. If the wave-length is one kilometre, $2\pi/n=\lambda/c=\frac{1}{3}\,10^{-5}$: so that if the rays are thus adapted over a vertical breadth of only a thousand metres the modulus of attenuation $\frac{1}{2}\kappa/c$ must increase downward across it, so that at the lower boundary it mounts to at least 10^{-6}, which means decay of amplitude in ratio e^{-1} after travelling only ten kilometres.)

To produce sensible bending of the rays without extinction, all action by conductive or other dissipation must thus be excluded. It would not suffice to say that the conductance has to become perfect, for then no waves could travel: the influence must be of dielectric type. A theory satisfying this criterion was hammered out in class-lectures at Cambridge on electric waves last February, and has been, in fact, already expounded in answers in the Mathematical Tripos much as it is proposed here to present it. The attention now excited by long-range free electric transmission, the most wonderful sudden practical evolution since the telephone, may attract the interest of a wider audience.

A sufficient cause for the increase of velocity, without dissipation, for waves travelling horizontally is, in fact, afforded by the free oscillations of ions even sparsely distributed in the very high regions of the atmosphere; though lower down their energy would be dissipated by collisions with the atoms and the travelling waves would be gradually quenched. Current is transmitted without any frictional loss across the vacuum of an electric valve by the jet of free electrons. On the other hand, in conduction in a metal the electrons or light ions get up speed at very rapid rate under the electric field, but at the end of each short free path they render up by collision part of the energy so acquired to the obstructing atoms of the metal, and this dissipation of the energy of the field is the measure of the electric resistance. For electric fields alternating at one-tenth of the rate of the waves of visible light, this process

of conduction is, as Rubens showed, fully established at each instant in metal—a fact which leads to some information as to the lengths of the free paths *. But for ions travelling in an intensely rarefied upper atmosphere the free path will be long, so that many alternations of the electric force of the field of radiation, even for long electric waves traversing the medium, may occur within the time of one ionic path. This involves that the travelling ions will in the main swing free under the influence of the waves and thus interact without dissipation of their energy, scattering by secondary radiation from the slowly oscillating ions being negligible : there will thus be an influence on the velocity of the waves without absorption. To suit the present explanation the change ought to be a substantial increase, notwithstanding the small number of the ions contributing to it in the ultra-rarefied upper atmosphere. And the reason is simple. The influence of an ion is measured (jointly with the time) by the mean value of the alternating velocity excited in it, and this for a given intensity of field is proportional to the period of the waves, so that for long electric waves the effect may be millions of times as great as for short waves of comparable energy—in fact, it involves the square of the wave-length. Waves of shorter length could travel in a lower layer without excessive absorption, where a greater number of ions may make up for their weaker oscillatory motion †.

In passing, one may note that the same principle will apply in general terms to the penetration of X-rays of high frequency across metals, especially of low atomic mass ; when the time over a free path amounts to several periods of the radiation, the absorption, which must be due mainly to free ions, will be much diminished and the radiation can penetrate

* *Cf.* Phil. Mag. August 1907.

† The only theoretical discussion which the writer has been able to find is by Dr. W. H. Eccles (Proc. Roy. Soc. p. 86, June 1912). A "Heaviside layer" above, so sharply bounded and so intensely conducting as to reflect the rays without penetration, is assumed, combined with an ionization of the middle atmosphere which bends them, but "in forming the equations it has been implicitly assumed that the ions are so heavy that they acquire only small velocities and make very small excursions under the action of the waves." A viscous term is inserted in the equation of motion of an ion ; if that term is annulled the formulæ must agree in form with those justified here for light ions of very long free path. The treatment is mainly by rays, and contains full discussion of the relevant observational material of that date, especially as regards stray radiations.

The diffraction theory of G. N. Watson (Proc. Roy. Soc. 1918, more recently studied) seems to make it unlikely that the ground can take any part in the actual transmission.

deeply—to a limit imposed mainly by simple dispersal or scattering, so proportional to the density of the atomic electrons: the Rubens experiments on reflexion of ultra-red light indicate a like result.

On general grounds the transparency of air for long electric waves would be expected to be great as compared with light; on account of the slow period molecular scattering is practically absent, and the mirage effects of local irregularities are negligible unless their extent is comparable with the wave-length (*cf.* p. 1032 *infra*).

The remark presents itself to contrast the finite free swayings of electrons or light ions in the ultra-rarefied gas of the upper atmosphere, which augment the speed of the exciting waves, with the finite swayings under the alternating attraction of the grid of a stream of electrons across a triode valve, which are thus partially trapped systematically by the grid and so establish its relay action.

There must thus be a layer high almost beyond the sensible atmosphere, within the auroral domain, in which a sheaf of horizontal electric rays, provided they are long enough, will travel without loss by absorption or scattering, concentration in this stratum being due to the potent influence exerted on the velocity of long waves by the free ions of small inertia interacting with them. But we have to suppose that the energy transmitted in this high stratum is being shed down to sensible degree all along the path, for the signals to be everywhere received. Introducing optical imagery, we can contemplate a special component ray-sheaf connecting the transmitter to every receiver situated along the path of the beam; these rays all gather together into a sort of caustic curve or layer up aloft, and so long as they are in it the energy travels onward without loss except by sideway spreading.

The question arises whether there can be enough energy to be thus showered down to receivers all over the earth. By a known principle a receiver collects energy over a range of order λ^2; thus the total energy put into the transmitting layer is reduced at the receiver in the order of magnitude $\lambda^2/4\pi a^2$, so that for a wave-length of a kilometre the amplitude of vibration is reduced to the order 10^{-4}, which is not excessive.

Propagation of Long Electric Waves in Ionized Highly Rarefied Gas.—One notes in the first place that the *aurora borealis*, due somehow to free ions, is displayed at a height of the order of fifty miles; this is ten times the height of

the homogeneous atmosphere, so putting aside effects of smaller order arising from change of temperature, the mean free path of the atoms would at that height be e^{10} times the value at the earth's surface, thus of the order of several centimetres. The number of molecules per cubic cm. would be $3.10^{19}e^{-10}$, or say 10^{15}.

Let us then consider the motion of an ion of charge e and mass m, with free oscillation superposed on its translatory motion, due to the alternating electric field of radiation passing over it expressed locally by an electric force

$$\mathrm{F}=\mathrm{A}\cos pt, \qquad 2\pi/p=\lambda/c.$$

For the oscillation thus superposed, all quantities being in electrodynamic units,

$$m\ddot{x}=e\mathrm{A}\cos pt, \qquad m\dot{x}=ep^{-1}\mathrm{A}\sin pt,$$

so that the amplitude is $ep^{-2}\mathrm{A}/m$. There are, say, N_0 effective similar ions per unit volume, each supplying its contribution $e\dot{x}$ to the electric flux; all ions, positive and negative, contribute in the same direction, but massive ones may be neglected. An electric current is thus produced of density C expressed in terms of the field F as

$$\mathrm{C}=-\mathrm{N}_0\frac{e^2}{mp^2}\frac{d\mathrm{F}}{dt}.$$

This current, of precisely the same type, adds, in the electrodynamic circuital equations of the exciting wave-train, to the usual Maxwellian dielectric "total current" of density $\frac{\mathrm{K}}{4\pi c^2}\frac{d\mathrm{F}}{dt}$, in which K is the static dielectric modulus of the medium and is practically unity for ordinary air. On adding them it comes out that the effective K is diminished to

$$\mathrm{K}'=\mathrm{K}-\mathrm{N}_0\frac{4\pi c^2e^2}{mp^2}.$$

If c' is the velocity of propagation, c'^{-2} is thereby altered from the value K/c^2, or say c^{-2} in the absence of ionization, to K'/c^2; so that

$$c'^{-2}=c^{-2}\left(1-\mathrm{N}_0\frac{e^2\lambda^2}{\pi m}\right).$$

This increase of speed from c to c' arising from free ions mounts with λ, so for long electric waves it would be sensible, notwithstanding extreme tenuity of the gaseous ions. It would usually be of no account except in metals for the short waves of light.

Roughly the ionic charge e is of order $\frac{3}{2}10^{-20}$ electromagnetic; taking a wave-length of one kilometre, λ is 10^5; and if the effective ions are electrons e/m is $\frac{7}{4}10^7$; the multiplier of c^{-2} on the right then becomes $1-10^{-3}N_0$.

What we are concerned for is that the rays should have a curvature exactly equal to that of the earth. The index of refraction is $\mu=\frac{c}{c'}=1-N_0\frac{e^2\lambda^2}{2\pi m}$, or, say here, $1-\frac{1}{2}10^{-3}N_0$. So the curvature of the rays, which is $-d\mu/dh$ (as *infra*) or $\frac{1}{2}10^{-3}\frac{dN_0}{dh}$, is not to fall short of $\frac{1}{2}\pi 10^{-3}$. For the present assumed data this condition of curvature requires $\frac{dN_0}{dh}$ to be about 3.10^{-6}, a value which must extend over the effective layer, which may be a considerable range of h, say 10^5 cm.; and this mounts up for the terminal value of N_0 to only about ·3 electrons or 5.10^2 hydrogen ions per cubic cm., whereas at the height of 50 miles there are still 10^{15} molecules of gas per cubic cm.

Bending of Optical Rays.—The directions of the wave-fronts are transverse to the rays, and consecutive rays meet at their centre of curvature: thus, considering as usual two adjacent rays of the coherent beam, at distance δn, as the time of transit is the same for both from one front to the next, and the element of path of the ray is $v\delta t$, we have $\delta v/v=\delta n/R$, so that the curvature R^{-1} of the ray is $d\log v/dn$, or here simply $-d\mu/dn$. Ordinary atmospheric refraction by the action of the molecules, according to this formula, as applicable to horizontal rays of light or electric rays, would be negligible at the heights here in question of the order of fifty miles; but at sea-level, where it is mainly due to temperature gradient, it would give a very substantial though insufficient contribution to the required amount of bending. For the refractive index of air for ordinary light, and also for long waves, is at sea-level 1·0003; and the curvature of a horizontal ray is $-\frac{d\mu}{dh}$, which as $\mu-1\propto\rho$ is $-3.10^{-4}\frac{1}{p}\frac{dp}{dh}$, if there is no gradient of temperature, or $3.10^{-4}\frac{g\rho}{p}$; wherein the speed of sound is $\left(1{\cdot}4\frac{p}{\rho}\right)^{1/2}=32400$ cm./sec. at 0° C., giving $\frac{p}{\rho}=\frac{2}{3}\left(\frac{13}{4}\right)^2 10^8$; so that $-\frac{d\mu}{dh}$ is $3.10^{-4}/\frac{2}{3}10^9.10^{-3}$ or 5.10^{-10}, which as the earth's radius is $\frac{2}{\pi}10^9$ amounts to as much as one-quarter of the

curvature of the earth. But actually the gradient of temperature $d\theta/dh$ affects this result by a factor $1+30d\theta/dh$ if h is measured in metres, and is the chief cause of mirage effects: for instance, the curvature of the ray would agree with that of the earth if the temperature increased upward by 1° C. for 9 metres *. These temperature variations of the ordinary index of refraction in the lower atmosphere would likewise affect long electric waves, were it not for the saving limitation that irregularities occupying only a small part of a wave-length would be of no account; while at a height say of 15 kilometres, where the density of the air is reduced seven times, the effect is in any case very slight. As already remarked, the effective stratum is too high for meteorological instabilities to affect it. But it will not, of course, be exactly horizontal: its height may be expected to be some function of the local solar time at the place.

Amplitude of Oscillations of Free Ions.—We have still to verify that the amplitude and time of the oscillation of an ion would not be too great, in comparison with its free path, to allow a large degree of freedom in its vibrations. The value of the amplitude is $\frac{e}{mp^2}$A, or $\frac{e\lambda^2}{4\pi^2mc^2}$A, where A is the amplitude of vibration of the electric force in the waves. If this field of force is V volts per cm. (which compares with ten volts per cm. for the field of full sunlight if it were coherent †) so that $A=10^8V$, the amplitude for an electron, with wave-length 10^5 cm. or one kilometre as above, is about $\frac{1}{2}10^3V$. It increases as the square of the wave-length. For a hydrogen ion it would be 1700 times smaller. Actually V is so small that even for an electron it fits amply within the gaseous free path at a height of fifty miles, where it is several cm. as above. But sufficient time

* *Cf.* Everett's exposition of James Thomson's theory, Phil. Mag. p. 169, Mar. 1873: or Rayleigh, 'Theory of Sound,' ii. § 288.

† Maxwell (Treatise, § 793) seems to have miscalculated the results. Solar radiation is 2 cal./min. where 1 cal. $=4{\cdot}18\times10^7$ ergs: for this intensity, if the radiation were coherent, the amplitude of its electric field would be as high as 10 volts/cm., and of its magnetic field ·034 or $\frac{1}{5}$ of the mean horizontal force in Britain. The pressure of the solar radiation is 500 grammes weight per square kilometre. But the solar natural radiation differs from the artificial radiations here discussed (which hardly occur at all in nature) in being a statistical aggregation from molecular origins and not one coherent undulation: for it, energy is the surviving fundamental datum, definite amplitudes of oscillation must be replaced by deviations from a steady average state of disturbance measured by a statistical mean square, and theory would be of entirely different form—that of natural radiation.

as well as space must be provided for this postulated regular forced oscillation of the ions. The period of a wave-length of one km. is $\frac{1}{3}10^{-5}$ sec.: the time for a molecular free path of 3 cm. would be of order rather more than 2 cm. divided by velocity of sound in the gas, which is, say, twenty times longer. But this is for air; for a hydrogen ion the time would be divided by at least 5, for an electron in thermal equilibrium perhaps by 200, unless its path were lengthened by passage through the atoms without much disturbance of its motion. Thus it is only in the ultra-rarefied upper atmosphere that the slow alternations of material ions under the influence of long electric waves would have time or space for many complete oscillations on one free path; and there Ohm's law would be wholly inapplicable.

If there are N_0 ions per cubic cm., each M times the mass of an electron, and the time in the free path is n times the period of the waves, of electric amplitude F_0, then in one second energy $\frac{F_0^2}{8\pi c^2}c$ passes across one sq. cm., while within one cubic cm. energy $\frac{N_0}{n}\frac{e^2\lambda^2}{8\pi^2 mc^2}F_0^2\Big/\frac{\lambda}{c}$ is dissipated in one second: by dividing, the modulus of absorption per cm. comes out $\frac{N_0\lambda}{n\,M}10^{-13}$. In the circumstances illustrated above n may be 10, N_0 is 2.10^3 hydrogen ions for which M is 1740, the wave-length λ is 10^5 cm., so that plane radiation would be reduced by ionic absorption acting alone in ratio e^{-1} in a path of ten thousand kilometres. This compares with the estimate given earlier of the effect of conductance.

We infer that the present type of explanation by a velocity of propagation increasing with height, which bends down the rays without undue absorption, is sound and reasonable for electric waves of the lengths usually employed, if only a very small proportion of the molecules of the upper air were ionized, so as to provide electrons or light ions, by the intense ultra-violet solar radiation. Across the region of the dawn the strata of ionization may be deranged: they may be deformed locally so much as to throw the concentrated horizontal sheaf of rays upward into space or else downwards to the earth so far that it cannot recover the horizontal direction in the new effective stratum. But if that stratum is deep, say a kilometre, such dislocation need not be complete. These considerations retain general validity when the strata of equal ionization are not exactly horizontal.

There seems to be some call here for closer scrutiny of

statistics as to the relation of range to wave-length: also as to whether reception is better or worse, or simply irregular, at times of dawn or sunset *. It is perhaps significant that "atmospherics" are reported to predominate at sunrise and sunset. It appears also † that there is increase of strength but diminished direction-finding at night: that in both respects North-South is superior to East-West: that winter is favourable in the Atlantic, and transmission over sea easier than over land.

Scrutiny of the induced electric moment of a molecule in a strong field is here incidentally suggested. For air at standard density the refractive index is of order $1+3.10^{-4}$: thus the induced polarity $\frac{K-1}{4\pi}F$ in electrostatic measure is $\frac{1}{2}10^{-4}F$ distributed over $\frac{3}{2}10^{19}$ molecules. If F is $\frac{1}{5}10^{5}$ volts per cm. (corresponding to a spark of 5 cm.), which is 60 electrostatic units, this gives a moment 2.10^{-22} for each molecule. As e is 5.10^{-10} electrostatic, the arm of the moment would be 4.10^{-13} cm., while the molecular radius is as much as 10^{-8}. Thus K would hardly fall away from being constant before the field approached 10^{6} electrostatic, and disruption would have set in long before.

Undulatory Propagation for a Thin Unchanging Sheaf of Rays.—The electric radiation to great distances thus involves a sheaf of rays whose breadth may be only a fraction of one of its long wave-lengths, which travels along a surface of constant index, while it has to remain concentrated without spreading either by refraction or by diffraction. The subject thus invites examination dynamically. The equation of propagation, neglecting now the terrestrial curvature of the strata, is of type

$$\frac{\partial^2\phi}{\partial x^2}+\frac{\partial^2\phi}{\partial z^2}=c'^{-2}\mu^2\frac{\partial^2\phi}{\partial t^2}, \qquad \mu^2=1+\psi(z),$$

where c' is the speed along the mid-front at which $\psi(z)$ vanishes. The type of waves here contemplated, with amplitude changing along the front as $f(z)$, is expressed by

$$\phi=f(z)\mathrm{F}(x-c't);$$

* It appears (Eccles, *loc. cit.* p. 97) that in transatlantic signalling the response, in fact, does attain a high maximum when either the receiver or the transmitter is in the dawn or the sunset: and other significant features are found.

† *Cf.* Prof. E. V. Appleton, Royal Institution Lecture, in 'Engineering,' May 30, p. 709.

but this must be further specialized for the analysis, into harmonic trains each of type

$$\phi = f(z)\cos m(x - c't), \qquad m = 2\pi/\lambda.$$

Then $$\frac{\partial^2 f}{\partial z^2} - m^2 f = -m^2\{1 + \psi(z)\}f,$$

or $$\frac{\partial^2 f}{\partial z^2} = -m^2\psi(z)f, \qquad \mu^2 = 1 + \psi(z).$$

For a disturbance with its parts keeping together as it travels, $f(z)$ must fall off on both sides of a maximum along $z=0$: that is, the graph of $f(z)$ must be concave to the axis of z, the condition for which is $\partial^2 f/\partial z^2$ negative; so that as the amplitude f is positive, $\psi(z)$ must be positive on both sides of the central plane. This is simply the familiar condition that the stratum is to be one of minimal index, close to which the rays must cling by virtue of the principle of minimal time of transit.

Over small range of z we may illustrate by taking

$$\mu = 1 + \mathrm{A}z^2:$$

the equation to determine the law of transverse intensity for such an unchanging layer of the wave-train is

$$\frac{\partial^2 f}{\partial z^2} + 2m^2\mathrm{A}z^2 f = 0,$$

which is amenable to simple graphical treatment.

The actual effective atmospheric stratum must, however, be curved to the earth's radius a, and the equation of wave-propagation of the curved sheaf of rays travelling along it is of type

$$\frac{\partial^2\phi}{\partial r^2} + \frac{1}{r}\frac{\partial\phi}{\partial r} + \frac{1}{r^2}\frac{\partial^2\phi}{\partial\theta^2} = c_0^{-2}\mu^2\frac{\partial^2\phi}{\partial t^2}, \qquad r = a + z,$$

where c_0 is the velocity along $z=0$ and μ is the index relative to that layer.

The type of waves travelling along it without spreading may as before be restricted to the harmonic form

$$\phi = f(z)\cos m(a\theta - c_0 t), \qquad m = 2\pi/\lambda.$$

As $r = a + z$ this gives

$$\frac{\partial^2 f}{\partial z^2} + \frac{1}{a+z}\frac{\partial f}{\partial z} - \frac{m^2a^2}{(a+z)^2}f + m^2\mu^2 f = 0.$$

Thus if $$g = (a+z)^{\frac{1}{2}}f, \quad \mu^2 = 1 + \psi(z),$$

$$\frac{\partial^2 g}{\partial z^2} + \left\{\left(\frac{1}{4a^2m^2} - 1\right)\left(1 + \frac{z}{a}\right)^{-2} + 1 + \psi(z)\right\}m^2 g = 0.$$

As before, the layer of transmission extends over the values of z which make the coefficient of y in this equation positive; for z small it approximates to

$$m^2\left(\mu^2-1+\frac{2z}{a}-\frac{3z^2}{a^2}+\frac{1}{16\pi^2}\frac{\lambda^2}{a^2}\right).$$

Thus substituting

$$\mu=\mu_0+\left(\frac{\partial\mu}{\partial z}\right)_0 z+\tfrac{1}{2}\left(\frac{\partial^2\mu}{\partial z^2}\right)_0 z^2+\ldots,$$

this equation in y takes the same form as the previous one in f, found as the analytical expression of the concentration of the rays for flat strata towards the straight ray of absolutely least time of transit, provided that when $z=0$ the curvature a^{-1} is equal to $-\left(\frac{d\mu}{dz}\right)_0$, as before obtained, and also $\mu_0\left(\frac{\partial^2\mu}{\partial z^2}\right)_0-\frac{2}{a^2}$ is positive.

It may be remarked that treatment of the cognate subject of optical mirage involves a like analysis *.

XCIX. *On Sommerfeld's and Landé's Rules for Classification of Terms and Zeeman Patterns in Spectra.* *By* W. M. Hicks, *F.R.S., Emeritus Professor of Physics, Sheffield* †.

WITHOUT doubt one of the most important advances in the analysis of spectra since Rydberg's discovery of the combination law is the recent extension ‡ of Sommerfeld's system of enumeration of species of term-types by Landé, combined with the completion of the latter's rules for predetermination of Zeeman patterns by the discovery of a formula for the splitting factor g, and the experimental establishment § of these rules by Back, and by Gieseler. The present communication contains I. a suggested change in form of the enumeration and the rules, and II. a discussion of the evidence for and against a rule, accepted by Landé, supposed to give the ratios of the separations in multiplets.

* *Cf.* Everett, *loc. cit.*

† Communicated by the Author.

‡ Sommerfeld, *Ann. d. Physik*, lxx. p. 32 (1923); Landé, *Zeits. f. Phys.* xv. p. 189 (1923).

§ Back, *Zeits. f. Phys.* xv. p. 206 (1923); Gieseler, *Ann. d. Phys.* lxix. p. 147 (1922).

I.

In order to bring out the essential nature of this method of classification I begin by recalling, in a quasi-historical order, the evidence by which the present enumeration has been arrived at. In doing this I assume the reader to be already acquainted with the classification itself.

It was early recognized that the observed series depended almost wholly on combinations of—or transitions between—selected sequences. In fact only combinations $sp, pd, df, \ldots$ or, in other words, if written in order s, p, d, f transitions only take place between neighbouring letters. This may be regarded as a true statement of normal conditions, if by "normal" is understood those transitions which take place most frequently. Transitions between terms of the same sequence are also common in certain types, e.g., p, p and d, d*. But transitions s, d † or p, f are rare, and seem to require a more severe excitation and in some cases the presence of an electric or magnetic field.

When Sommerfeld gave his extended theory of quantization of the generalized coordinates of a system, and applied it to a special model of a single electron circulating round a sheathed nucleus, he deduced, as is well known, the term-formula $N/\{m+\mu+\alpha/(m+\mu)^2\}^2$, in which m is the sum of the radial and azimuthal numbers and μ, α are functions of the azimuthal alone. It was natural therefore at once to draw the inference that the different types were determined by their azimuthal quanta. The possibility of a zero value of m was excluded as it was supposed that an electron oscillating in a line through the nucleus was impossible. Hence a zero azimuthal number is also excluded. Consequently s, p, d, f or succeeding g, h, ... were supposed to

* $p1-pm$ sets are so common in arc spectra as to be expected when searching a spectrum for P series, for which they are used to establish doubtful P allocations, or to extend the series beyond observed regions. All multiplets whose lines show a common Z.P = 0/3/2—L category of my 'Analysis'—are due to transitions between terms of the same type, and they occur as strong sets not only in all the spectra of the alkaline earths, but in many others (Popow) whose series relations are not yet fully established. Similarly d, d multiplets occur in all the alkaline earths. As striking instances may be adduced a dd multiplet in Mn and 0,3/2 multiplet in Cr. Their lines occur in the lowest temperature furnace spectra of King.

† Messrs. Foote, Mohler, and Meggers (Phil. Mag. xliii. p. 459) find strong lines $s1-d2$ in Na and K in cases where electric or magnetic fields are excluded, also seen by Datta (Proc. Roy. Soc. 101. p. 545) as absorption lines. But although showing that the exclusion of such transitions is not absolute, they do not affect the general statement that such are rare, *i. e.* abnormal in the sense above.

depend on successive azimuthal numbers 1, 2, 3 .... Thus a term-type is definitely fixed by an expression n_k. We need not stop to consider difficulties in connexion with assignation of azimuthal quanta to term-type, as that is outside our present subject, but if we decide to enumerate types by successive numbers, these numbers 1, 2, ... are the simplest. In this case the observational facts referred to above give the normal transitions by

$k \longrightarrow k-1$, or $k+1$ and $k \longrightarrow k$ (restricted cases). Rule I.

Bohr deduces from his principle of correspondence that $k \longrightarrow k$ is impossible if k is an azimuthal number. The experimental facts indicated above would seem to require some modification either in the principle of correspondence or in the azimuthal quality of the k.

The next step is to classify the satellite effect, which shows the existence of more than one species in a type. Thus in doublets there are one s, two p, d, f, and in triplets one s, three p, d, f—at least in elements of group II. Sommerfeld co-ordinates these by a new set of successive integers *—now written j—an individual term being now represented by n_{kj}. Here the experimental fact ruling conditions is that we never find transitions from more than three species of one type to one of another (see, however, Note at end). In other words, in the arrangement of any multiplet in regular order the lines appear in sets of three only. Thus, *if* we decide to use successive integers in classifying species of types, we get Sommerfeld's transition rule

$j \longrightarrow j+1,\ j,\ j-1.$ . . . Rule II.

We might equally well decide to use say successive even numbers, when the rule would be $j \longrightarrow j+2, j, j-2$, or any other regular succession. The important fact now emerges, that after settling this successive order, all the j of all the types depend uniquely on the value chosen for one, say the singlet or doublet s, which is a type of only one species. It will be sufficient here to indicate how this results without going into actual details. Consider first the case of elements which have an even number of external or removable electrons and which produce singlets; triplets—(Rydberg's rule).—In the singlet all the terms are single. We decide (*i. e.* Sommerfeld) to give $j = 0$ to s'. We find a relation

* The attempts of Sommerfeld and his associates to explain these numbers by picture models are another matter, and, however useful and suggestive, tend to obscure their experimental origin. We shall refer to them as j values instead of internal quanta, thus leaving their real origin an open question, as indeed it is.

between singlets and triplets by the $s'-p_2'''$ lines, with no $s'-p_1'''$ and with $s'-p_3'''$ weak or requiring excitation by the spark, *i. e.* not normally radiated. It is necessary then, if rule II. holds, that the j for $p_{1.2.3}$* should run 2, 1, 0. This excludes the combination $s'p_1'''$ but allows the others. To meet the exclusion of $s'p_3'''$ Landé has added an additional rule

$$j = 0 \longrightarrow j = 0 \text{ forbidden}, \quad . \quad . \quad . \quad . \quad II_a.$$

and it is suggestive that in the new manifolds recently discovered the corresponding two lines—e. g. $s^5-p^7{}_{2.3}$, where no $j = 0$ can be in question, both exist as strong lines in the arc. The rule is justified also as it is required to reproduce the observed combinations in the L—or 0/3/2—multiplets in which p_3-p_3 (i.e. $j = 0$ to $j = 0$) is not observed. With p''' settled as 2.1.0, the D sets necessitate 3.2.1 for d_1, d_2, d_3 and the F 4, 3, 2 for f_1, f_2, f_3, in order that rule II. may exclude $p_2\ d_1$, $p_3\ d_1$, $p_3\ d_2$ and allow the others, etc.

It will be noticed that where p is single so are d, f, when p is double so are d, f, and when p is triple so are d, f. This fact led Sommerfeld to formulate a statement which he called the "permanency of multiplicity," which represented facts as known at the time. But in the spectrum of Mn and Cr Catalan in 1922 found series in which s was single, p triple, and d fivefold. These discoveries revolutionized ideas in spectral classification and at the hands of Landé have given us for the first time definite tests of term character, and the power of predetermining Zeeman patterns.

Catalan's discovery—at once extended by other investigators—showed that we must add yet another category of spectral terms, and that groups of $s\,.\,p\,.\,d\,\ldots$ exist other than those of singlet, doublet, and triplet groups. Landé gave precision to Sommerfeld's "permanency of multiplicity" by referring the statements to the particular multiple group. The multiplicity of the terms increases by two successively up to a permanent value determined by the attainment of a j value $= 0$. Thus in the quintet system s is single, p triple, d fivefold (here $j = 0$ for d_5) with f and all terms beyond fivefold. Thus each group can be classed according to its permanent multiplicity. Landé denotes this by r—the term by n^r_{kj} say $n\,(k,j,r)$—and again attached a name, Rumpfquantumzahl, which depended on a picture model which may possibly be discarded with further knowledge. I shall refer

* We keep the old numeration where p_1 is the term which gives the most intense line and which corresponds to the highest energy level, or lowest energy value.

to it as its r class, and propose to denote the group as a manifold *. Thus a fivefold group contains s with singlet, p with triplet, $d.f.g$ ... with quintic multiplicities. The transition rule is

$$r \longrightarrow r+2,\ r,\ r-2. \quad . \quad . \quad . \quad \text{Rule III.}$$

It may be noted that Landé's j classification is uniquely determined (subject to choice of j for s in the four and five folds) by observed data. Just as the relations between those of the one and three folds are related by the intercombinations s^1-p^2, so those of the five and seven folds, and those of the six and eight folds are connected by intercombinations of $s^5-p^7{}_{2,3}$ in Cr and $s^6-p^8{}_{2,3}$ in Mn. At present there are no observational data to relate the three and five folds, but Landé's classification meets this by choosing j for s^5 by analogy. We may note that in group II. with two external electrons we have one- and three-fold groups, in group VI. (Cr, Mn^+) with six, five- and seven-folds, in group VII. (Mn, O^+) with seven, six- and eight-folds, in group I. with one, no- and two-folds. We are justified, therefore, in inferring at least provisionally that an atom—neutral or ionized—with n external electrons radiates in series depending on terms in $n-1$ and $n+1$ folds, and more copiously in the $n-1$. But that such a rule is not exclusive is shown by the fact that O exhibits a 0/3/2 multiplet of threefold type (see also Note at end).

Rule III. forbids a transition between even and odd manifolds, which accords with the well-known fact that in any one element such manifolds belong to different radiating atoms. The two systems for even and odd manifolds are therefore quite independent and may start from different initial j for the singlet s. The choice of 0 for s^1 and 1 for s^2 is therefore arbitrary, as well as the intervals between successive j. For instance it is open to us to take successive even numbers, starting from 0 for odd folds, and successive odd numbers starting from 1 for even folds. The transition rule II. would then be

$$j \longrightarrow j+2,\ j.\ j-2. \quad . \quad . \quad . \quad \text{Rule II}'.$$

In this way the oddness or evenness of j would refer to the oddness or evenness of the number of external electrons associated with the transition-electron. Further, with this numeration transitions between odd and even folds would also be forbidden by rule II′. This is not by itself sufficient inducement to change Sommerfeld and Landé's basis of

* Permanent multiplicity is too long, and multiplicity by itself is needed to define that of a term type.

numeration, but the inducement is strengthened when the greatly increased simplicity in Landé's rules for the predetermination of Zeeman patterns is considered. This is indicated by putting side by side the corresponding rules under the two systems. The j, g values for the two terms of a combination are represented by j_x, g_x and j_y, g_y with $j_x \geqq j_y$. In each scheme the j and g are to be supposed expressed in their respective ways.

	Old Scheme.	*New Scheme.*
1.	Equation for g.	
	$\frac{3}{2}+\frac{r^2-(2k-1)^2}{8j(j+1)}$ for odd folds $\frac{3}{2}+\frac{r^2-(2k-1)^2}{2(2j-1)(2j+1)}$ for even	$\frac{3}{4}+\frac{r^2-(2k-1)^2}{4j(j+2)}$
2.	Rule for multiplying factor—m in mg.	
	m = successive integers from j to $-j$ including 0 for odd folds m less by $\frac{1}{2}$ excluding 0 for even	m = integers from j to $-j$ at intervals of 2
3.	Components follow one another at intervals e =	
	g_x-g_y	$2(g_x-g_y)$
4.	The spread between the strongest components. This depends on whether j_x, j_y are different or equal.	
	j_x, j_y different.	
ϖ.	0 for odd g_x-g_y for even	0 for odd $2(g_x-g_y)$ for even
σ.	$2(j_xg_x-j_yg_y)$ odd $(2j_x-1)g_x-(2j_y-1)g_y$ even	$2(j_xg_x-j_yg_y)$
	j_x, j_y equal.	
ϖ.	$2j(g_x\sim g_y)$ odd $(2j-1)(g_x\sim g_y)$ even	$2j(g_x\sim g_y)$
σ.	$2g_x$ and $2g_y$ odd g_x+g_y even	$4g_x$ and $4g_y$ odd $2(g_x+g_y)$ even
5.	Number of components.	
ϖ.	$2j_y+1$ odd $2j_y$ even	j_y+1
σ.	$2(j_x+j_y)$ odd $4j_y$ even $(j_x>j_y)$ $2(2j_y-1)$ even $(j_x=j_y)$	j_x+j_y

The greater simplicity of the new arrangement is clear. Possibly also it may render it possible to dispense with half quanta in the picture model illustrating the classification. The establishment of Landé's rules for the Zeeman pattern by the experimental work of Back shows conclusively that the Sommerfeld-Landé's $k.j.r$ method of enumeration corresponds in some way to an ordered arrangement within the atom. It is possible that additional sub-classes may be necessary with more complete knowledge. Such a necessity is suggested by observational data which appear to exhibit more than one n (k, j, r) term, but until an analysis of these new spectra has been made no definite conclusion can yet be drawn.

The statements as to the number of ϖ and σ components require a limitation. They are true provided none of the calculated components coincide. This may happen in two ways:

(*a*) $g_x = g_y$. In this case all the ϖ and all the σ coalesce to form a triplet with a σ shift of g. As an example is the L category of multiplets ($r = 2k-1$) in which the Z.P. reduces to the triplet 0/3/2.

(*b*) This affects only the number of σ components. The magnitude of the shifts on one side of the original line may be regarded as given by all the arrows in a Landé diagram which slope in one direction, no regard being paid to sign. Using the new scheme of numeration the extreme shift is $j_x g_x - (j_x - 2) g_y = 2g_x + (j_x - 2)(g_x - g_y)$. All the shifts are then given by

$$2g_x + (j_x - 2)(g_x - g_y) - n \,.\, 2(g_x - g_y),$$

where n ranges from 0 to $\frac{1}{2}(j_x + j_y) - 1$. Should any of these be numerically equal (opposite sign), the corresponding components in the pattern will coincide. The condition is therefore

$$2g_x + (j_x' - 2 - 2n)(g_x - g_y) = -\{2g_x + (j_x - 2 - 2n')(g_x - g_y)\},$$

whence $$n + n' = j_x - 2 + \frac{2g_x}{g_x - g_y}.$$

Hence a necessary condition is that $2g_x/(g_x - g_y)$ is integral $= p$ say. But $n + n'$ is necessarily less than the sum of the maxima of n, n', i. e. $n + n' < j_x + j_y - 2 > 0$. Hence

$$j_x - 2 + p < j_x - 2 + j_y > 0,$$

$$2g_x/(g_x \sim g_y) < j_y ;$$

or in Landé's system

$$2g_x/(g_x \sim g_y) < 2j_y \text{ for odd folds, } 2j_y - 1 \text{ for even.}$$

As an instance may be taken $n^3{}_{4.4}-n^3{}_{5.3}$, or say in the old notation $f_1'''-g_3'''$ *. Here using Landé's numeration

$$j_x=4,\quad g_x=\tfrac{5}{4},\quad j_y=3,\quad g_y=\tfrac{3}{4},\quad p=5<2j_y.$$

The Landé diagram is

$$-\tfrac{20}{4}\cdots\cdots\quad -\tfrac{5}{4},\quad 0,\quad \tfrac{5}{4},\quad \tfrac{10}{4},\quad \tfrac{15}{4},\quad \tfrac{20}{4},$$

$$-\tfrac{9}{4}\cdots\quad -\tfrac{3}{4},\quad 0,\quad \tfrac{3}{4},\quad \tfrac{6}{4},\quad \tfrac{9}{4},$$

whence the Z. P. follows at once as

$$0.2.4.6/1.1.3.5.7.9.11/4,$$

with six side σ components instead of seven as given by the rule 5 above. There are many cases in which the first condition, $p=$integral, is satisfied, but in a few only are the j large enough to satisfy the second.

II.

Landé enunciates a theorem relating to multiplet separations which appears as a deduction from the model. It is that the separations between the species of a term-type are proportional to $\frac{1}{2}(j^2-j'^2)$ in even folds or $\frac{1}{2}(j-j')(j+j'+1)$ in odd. In other words the successive separations are proportional to $\frac{1}{2}(j+j')$—$(j=j'+1)$—for even and $\frac{1}{2}(j+j'+1)$ for odd (in new system $\frac{1}{2}(j+j'+2)$ for all folds). Consequently they run

$$3:5:7:\quad \text{in even folds.}$$

$$1:2:3:\quad \text{in odd}\quad ,,$$

In support of this rule he has adduced some data which lead him to think that the statement is approximately true. If the rule is a true statement, its significance is so important that I propose to examine how far the data at our disposal support it, or the contrary. In treating the data the ratio of the separations will be given in terms of the smallest, treated as 1.

In the first place we should remember that the rule as stated cannot be true with absolute exactness, for these separations have their source in changes in the denominator of the Rydberg term-function, and it is to these displacements that any such rule would be applicable. Nevertheless, the changes in the ratios of the actual separations (ν_1, ν_2 ...) from those of the corresponding denominator displacements

* Here g refers to term-type, not splitting factor.

(Δ_1, Δ_2 ...) will be very small, unless the separations themselves are considerable *. The effect is to diminish the rate at which the separations increase, below that of the real changes (Δ . .), except where as in the almost unique case of Mn the displacements are of the opposite sign, when the rate is increased. In the present case, however, the observed separations are not so large as to produce an essential modification.

If a set of separations are in a ratio given by an arithmetic series, as here, the fact shows itself at once by the constant differences between them. This test is of course not applicable to triplets. We find a few cases only in the lately recognized multiplets, so that their fewness is rather *à priori* against the rule as applicable to multiplets with any closeness.

In considering the data we must also remember that throughout a series, the separations tend to keep the same ratio approximately for all orders. If therefore there is agreement with the rule for the first order, it is no additional evidence in favour if succeeding orders are also adduced, nor on the other hand is the evidence against increased by considering all the orders when the first is in disaccord. This consideration applies to the case of the F series in Al^+, adduced by Landé, in which close agreement is found for nine successive orders.

The question also will arise as to what is to be taken as approximate agreement. For instance, say theory requires a ratio $3/2=1{\cdot}5$ and observation gives $1{\cdot}66$. At first sight this might be taken as a rough agreement, but as a fact it corresponds to a ratio 5 : 3, and really contradicts a theoretical 3 : 2. It must be remembered that the observed ratios are definite up to at least the third decimal place. We should then estimate agreements as between numbers of three significant figures. Further, it is not legitimate to average two numbers deviating equally from those expected, as for instance Back † with an expected ratio 7 : 5 and two observed ratios 7 : 4·3 and 7 : 5·7. These are probably really cases of 4·33 and 5·67 corresponding to exact ratios 21 : 13 and 21 : 17.

With these preliminary remarks we proceed to the actual data, taking those of each manifold by themselves—the odd first. The two-folds or doublets do not of course enter.

* *E. g.* in Hg, $\nu_1 : \nu_2 = 4630{\cdot}467 : 1767{\cdot}279$ (R/A) = 2·620. $\Delta_1 : \Delta_2 = 87819{\cdot}08 : 30008{\cdot}03 = 2{\cdot}927$.

† *Zeits. f. Phys.* xv. p. 223.

After each term symbol are given the j values and next the Landé ratio.

Three-folds.

p^3, $j=2.1.0$		$2:1=2$					
A	2·37	Be	3·57			Al^+	2·08
Kr	2·31	Mg	2·03	Zn	2·045	O	2·52*
X	2·18	Ca	2·03	Cd	2·16	Se	2·32?
Ra Em	2·03	Sr	2·10	Eu	2·62		
		Ba	2·37	Hg	2·62		

* from a triplet 0/3/2 multiplet (Paschen and Back, *Ann. d. Phys.* xxxix. p. 914). Its separations 195·83, 77·59 are much larger than those of the generally accepted OP, which is definitely a five-fold set. The generally accepted SeP, also with large seps : is also possibly a three-fold P, and if so comes in here.

d^3, $j=3.2.1$		$3:2=1·5$					
A	?	Mg	?	Zn	1·17	Al^+	1·30
Kr	1·69	Ca	1·44	Cn	1·64		
X*	1·65; 1·66	Sr	1·68	Eu	1·66		
Ra Em*	1·68; 1·75	Ba	2·10; 1·65†	Hg	1/1·71§		

* two independent D sets. † a second incomplete D set—the accepted D is very irregular. § The well-known abnormality in Hg with inverse to normal ratio.

f^3, $j=4.3.2$		$4:3=1·33$			
Sr	1·43	Cd	?	Al^+	1·32*
Ba	1·2	Eu	1·77		
		Hg	?		

* the largest f sep : it gives the best agreement with Landé.

Multiplets.

A. *dd.* $j=3.2.1$	$3:2=1·5$	B. *dp.* $j=2.1.0$	$2:1=2$
Ca	1·50	Ca	2·46
Sr	1·51	Sr	3·18; 2·53
Ba	1·52; 1·66*	Ba	4·07

* Error in 'Analysis,' p. 68. Should be 448·3 : 339·5=1·66.

L. *pp.* $j=2.1.0$	$2:1=2.$		
Be	1·50	Al^+	1·92
Mg*	2 : 1	O	1·89
Ca	1·84, 1·94		
Sr	1·32†, 1·94		
Ba	1·753†... 2·407		

* Paschen and Götze give this as a 0/3/2 set, which must be very doubtful. The lines are portions of $S_{1.2.3}$ (5) and (Δ_2) $S_{1.2.3}$ (5) ('Analysis,' p. 263). Their allocation gives a denominator 5·33 quite out of step with others of this type.

† The single line for p_2-p_3' in Sr given by Götze (*A. d. Phys.* lxvi. p. 291) is clearly anomalous. There appears some analogy with Ba which gives two mutually displaced lines, with a separation giving a possible ratio close to 1·9. See 'Analysis,' pp. 223, 224.

Five-folds.

p^5, $j=3.2.1$ * 3 : 2=1·5

O	1·81	1·71	Cr	1·567; p^a, 1·463; p^b, 1·18
S	1·55	1·55	Mn^+	1·571
Se	2·32	1·30	Cl^+	1·674

* Analogous triplets in O. S. Se.

d^5, $j=4.3.2.1.0$ 4 : 3 : 2 : 1

Cr	3·538 : 2·794 : 1·943 : 1
Mn^+	4·593 : 3·195 : 2·047 : 1

L or 0/3/2 multiplets, dd' in Cr

1·702 : 1·513 : 1·384 : 1
3·216 : 2·580 : 1·862 : 1
3·490 : 2·811 : 1·958 : 1

f^5, $j=5.4.3.2.1$ 5 : 4 : 3 : 2 =2·5 : 2 : 1·5 : 1

Cr* ...	2·433 : 1·971 : 1·491 : 1
	2·602 : 2·138 : 1·775 : 1
	2·355 : 1·959 : 1·265 : 1

* Gieseler arranges the three sets as successive orders of F. But as all the separations are of the same order of magnitude, this may be doubtful—all three are therefore given.

Seven-folds.

p^7, $j=4.3.2$ 4 : 3=1·333 : 1

Cr	1·379.	p^a	1·258
Mo	1·741;		1·39
Mn^+	1·490		

d^7, $j=5.4.3.2.1$ 5 : 4 : 3 : 2=2·5 : 2 : 1·5 : 1

Cr	1·56 : 1·24 : 1·19 : 1
Mo	2·77 : 2·12 : 1·49 : 1
	*2·758 : 2·284 : 1·761 : 1

* from a multiplet $p-d$.

Four-folds.

p^4, $j=3.2.1$ 5 : 3=1·666 | d^4, $j=4.3.2.1$ 7 : 5 : 3=2·333 : 1·666 : 1

Mn *	1·750	O^+	1·51
Mn*	2·541 : 1·715 : 1		

* Back's new pd multiplet.

Six-folds.

p^6, $j=4.3.2$ 7 : 5=1·400 : 1 | d^6, $j=5 \ldots 1$ 9 : 7 : 5 : 3=

[3·000 : 2·333 : 1·666 : 1

Mn S^6	1·226 : 1	Mn, pd (I)	3·151 : 2·337 : 1·670 : 1
S^{6a}	1·635 : 1	pd (II)	3·346 : 2·470 : 1·697 : 1
pd (III) *	1·574 : 1	dd (IV)	2·600 : 2·199 : 1·295 : 1
dp (V)	1·435 : 1	dd (VII)	3·385 : 2·622 : 1·755 : 1

* Roman numerals refer to Catalan's multiplets in his order.

f^6, $j=6 \ldots 1$. 11 : 9 : ... : 3=3·666 : 3 : 2·333 : 1·666 : 1

Mn F^6 (VI.) ..... 4·040 : 3·345 : 2·500 : 1·715 : 1

Eight-folds.

p^8, $j=5.4.3$ $9:7=1{\cdot}286:1$	d^8, $j=6:5\ldots:2$ $11:9:7:5=$ $[2{\cdot}200:1{\cdot}800:1{\cdot}400:1$
Mn P^8 ..... $1{\cdot}343:1$	Mn D^8 ..... $2{\cdot}651:1{\cdot}93:1{\cdot}31:1$

In forming a judgment on the foregoing perhaps too much weight should not be given to any adverse evidence depending on the extra p, d terms brought in by the dd', pd', pp' multiplets. Their Zeeman patterns show that they are typical p, d terms ; they cannot be higher orders of the $p(1)$, $d(2)$ terms of the P, D series ; but their real nature is still to be found * and may require as noticed under I. a new category. Also little weight can be given to one or two close agreements amongst a larger number of adverse ones in the same set. We find extremely close agreement in the three fold extra d—given by the A multiplet $d-d'$. The three-fold series d, however, clearly point to a normal ratio of 5 : 3. The satellites of a first D set are very subject to displacement, and it is perhaps significant that if we use the next order D(3) in Ca and Sr the ratios become 1·507, 1·532 respectively, *i. e.* agree with Landé.

The data taken as a whole speak definitely against the rule as even an approximate one. But we should notice the close general agreement that when the rule gives close ratios so do the observed, and when wide, wide. This appears a very strong argument that there is some connexion with reality behind the rule, such for instance as would occur if the j enter in the way supposed but loaded with some other physical constant—or classifying number.

October 14.

[*Note added in proof sheets.*—Since writing the above I have become acquainted with the paper by Walters on multiplets in Fe (Jour. Wash. Acad. Sc. xiii. 243) and another by Gieseler and Grotrian (*Zsch.-f. Phys.* xxii. 245) in which the nature of the term-types in Walters' multiplets are considered. We find in Fe cases of transitions from one term-species to four others. It is the only case known to me where the j-transition rule is contravened. Further we

* I suspect they involve link connexion. That of the Ba L or 0/3/2 is certainly so connected. The line $n=24737$ in Mn—Cat : IV a d_1-d_1' line—is linked to another $n=25040$ by $392{\cdot}91=\nu_1+\nu_2-{\cdot}05$, and no p term to produce this can occur in the former. Also the sets on p. 157 of his paper beginning with 30851·44, 30722·19 are separated by exact ν_2—again with no p term present.

find the multiplets based on a five manifold, and not as we should have expected from the law suggested above, chiefly on seven- and nine-folds. Gieseler and Grotrian give the data referring to Landé's separation law. In the five-folds they find good agreement in one p, in one d out of four, fair agreement in one f out of two. In the three-folds good agreement in one f out of two and in one g. In a note added in the proof they give another F^5 multiplet. Here the separation ratios are 3 : 2·21 : 1·56 : 1 compared with a theoretical 2·5 : 2 : 1·50 : 1.

C. *Note on Vapour Pressures of Monatomic Substances.*

By Alfred C. Egerton *.

FOR the expression of vapour pressure results, various formulæ have been used as approximations to the thermodynamic formula

$$\log_e p = -\frac{\lambda_0}{RT} + \frac{C_p{}^g}{R}\log_e T - \int_0^T \frac{dT}{RT^2}\int_0^T C_p{}^s\, dT + \text{constant}.$$

The three-constant Kirchhoff formula

$$\log p = -\frac{B}{T} - C\log T + A,$$

or the four-constant Nernst formula

$$\log p = -\frac{B}{T} + 1{\cdot}75\log T - \frac{\epsilon T}{R} + A,$$

are frequently employed. The object of the present paper is to point out that a simple linear equation can be used to express the measurements of the vapour pressures of monatomic substances with about equal accuracy.

The specific heat of the solid at ordinary temperatures is about 3 R, while that of the vapour is 2·5 R, so that C in the Kirchhoff formula becomes 0·5, but this only holds in the region where Cv is 3 R.

It is a necessary consequence of the above thermodynamic formula that a linear relationship $\left(\log p \text{ plotted against } \frac{1}{T}\right)$ should approximately hold.

* Communicated by the Author.

If $$\left[\frac{C_p^g \ln T}{R} - \int_0^T \frac{dT}{RT^2}\int_0^T C_p^s dT\right]$$

is evaluated, using the Debye formula for a range of values of $\frac{\beta\nu}{T}$, the differences ($\triangle$) closely approach a maximum value which is fairly constant over a wide range of temperature. This range is that over which the vapour pressure is appreciable. The vapour pressure equation of a solid substance with monatomic vapour becomes, therefore,

$$\log p = -\frac{\lambda_0}{RT} + (\triangle + C) = -\frac{B}{T} + A'$$

(C being the chemical constant). Table I. gives $\triangle$ for various values of $\beta\nu$ and T.

The values of $\frac{1}{2}\log T$ given in the first column show greater divergency from constancy.

The change with temperature of the integrated value for the correction of Cv to Cp is insufficient to affect the conclusion.

It may be mentioned that λ is a maximum where $\frac{\beta\nu}{T} = 2$ (see Phil. Mag. xxxix. p. 14, 1920); below this temperature vapour pressures would become greater than indicated by extrapolation of the linear relation, but in all such cases the pressures would be immeasurably small.

To take the case of cadmium, the theoretical equation between 400° K. and the melting point 594° K. would lead to the formula (where $\beta\nu = 168$ and chemical constant 1·487):

$$\text{at } 400^\circ \text{K.} \log p = -\frac{\lambda_0}{RT} + 6{\cdot}505 - 1{\cdot}762 - 0{\cdot}029 + 1{\cdot}487$$
$$= -\frac{\lambda_0}{RT} + 6{\cdot}201,$$

$$\text{at } 594^\circ \text{K.} \log p = -\frac{\lambda_0}{RT} + 6{\cdot}935 - 2{\cdot}210 - 0{\cdot}052 + 1{\cdot}487$$
$$= -\frac{\lambda_0}{RT} + 6{\cdot}159.$$

Taking $\log p$ mm. $= -2{\cdot}33$ at 523° K., the thermodynamic equation might be expressed very closely by

$$\log p \text{ (atmos.)} = -\frac{5954}{T} + 6{\cdot}287 - 2{\cdot}14 \,.\, 10^{-4} T.$$

Table I.

			Differences △.								
T° K.	$\frac{1}{2}\log T$.	$2{\cdot}5\log T$.	$\beta\nu=20$.	$=50$.	$=100$.	$=200$.	$=300$.	$=400$.	$=500$.	$=1000$.	$=2000$.
10	0·5	2·500	2·1194	2·4401	2·4916						
20	0·65	3·2525	2·3614	2·9875	3·1926	3·2441	3·2500				
50	0·8495	4·2475	2·4311	3·3564	3·8669	4·1446	4·2106	4·2311	4·2391		
100	1·0	5·0000	2·3749	3·4284	4·1089	4·6194	4·8106	4·8971	4·9101	4·9916	
200	1·1505	5·7525	2·2727	3·3919	4·1809	4·8614	5·1914	5·3719	5·4875	5·6926	5·7441
400	1·3010	6·5052	2·1476	3·2746	4·1446	4·9336	5·3511	5·6141	5·7828	6·2402	6·4453
600	1·3891	6·9455	…	…	4·0668	4·9149	5·3739	5·6756	5·8876	6·4526	6·7921
800	1·4515	7·2577	…	…	4·0271	4·8971	5·3626	5·6861	5·9222	6·5550	6·9927
1000	1·5000	7·5000	…	…	4·0202	4·8749	5·3557	5·6836	5·9284	6·7089	7·1194
1500	1·5880	7·9402	…	…	…	4·7861	5·3151	5·6582	5·9096	6·6703	7·2853
2000	1·6505	8·2525	…	…	…	4·7727	5·2492	5·6274	5·8919	6·6809	7·3614
3000	1·7385	8·6927	…	…	…	4·6883	5·2129	5·5452	5·8140	6·6621	7·4228

The following Table (II.) shows that this equation leads to very nearly the same results as the empirically determined linear equation $\log p$ atmos. $= -\frac{5891}{T} + 6{\cdot}053$.

TABLE II.

T.	log p.		
	Thermodynamic.	Empirical.	Observed.
421·9	−5·035	−5·028	−4·96
482·6	−3·273	−3·272	−3·28
513·6	−2·536	−2·536	−2·54
523·0	−2·329	−2·329	−2·33
532·5	−2·128	−2·129	−2·12
545·6	−1·863	−1·864	−1·88

At high and low temperatures greater divergencies might be expected, but it is possible to represent over the range of the measurements the vapour pressure of solid argon and of tungsten by a linear relation as well as by any other equation, as the following figures illustrate :—

TABLE III A.—Vapour Pressure of Argon (Solid).

T° K.	I.	II.	III.	IV.
65·49	1·3418	1·3387	1·3414	1·3395
66·16	1·4041	1·4000	1·4024	1·4016
69·43	1·6809	1·6944	1·6941	1·6996
70·49	1·7727	1·7843	1·7833	1·7893
71·95	1·8891	1·8988	1·8972	1·9044
73·93	2·0483	2·0541	2·0517	2·0590
75·50	2·1644	2·1645	2·1623	2·1695
76·69	2·2477	2·2544	2·2515	2·2605
77·48	2·3023	2·3035	2·3010	2·3093
79·06	2·4075	2·4098	2·4073	2·4146
80·60	2·5068	2·5079	2·5057	2·5111
81·42	2·5569	2·5569	2·5551	2·5600
82·75	2·6394	2·6428	2·6408	2·6449
83·21	2·6668	2·6673	2·6657	2·6697
83·93	2·7095	2·7082	2·7070	2·7100

Column I. Measurements by Born (*Ann. d. Phys.* lxix. p. 473, 1922).

Column II. $\log p = -\frac{408{\cdot}80}{T} + 7{\cdot}5811$.

Column III. $\log p = -\frac{366{\cdot}87}{T} + 1{\cdot}75 \log T - {\cdot}0028293\,T + 1{\cdot}0698$.

Nernst formula used by Born.

Column IV. $\log p = -\frac{401{\cdot}88}{T} + 2{\cdot}5 \log T - F(\beta\nu) + {\cdot}0000142\,T^2 + 3{\cdot}671$

taking $\beta\nu = 85$, $\lambda_0 = 1840$. $C = 3{\cdot}67$.

TABLE III B.

Vapour Pressure of Tungsten.

T° K.	I.	II.	III.	IV.
2440	−6·903	−6·990	−6·972	−6·648
2522	−6·426	−6·370	−6·359	−6·113
2300	−4·583	−4·544	−4·542	−4·535
2930	−3·900 −3·766	−3·809	−3·814	−3·903
2925	−3·929 −3·798	−3·836	−3·842	−3·928
3136	−2·673	−2·772	−2·781	−3·014

Column I. Measurements of Langmuir (*Phys. Zeit.* xiv. p. 1273, 1913).

Column II. $\log p = 15{\cdot}502 - \frac{47440}{T} - 0{\cdot}9 \log T.$

Column III. $\log p = 11{\cdot}920 + \frac{46100}{T}.$

Column IV. $\log p = -\frac{41{\cdot}311}{T} + 7{\cdot}835 - 1{\cdot}78\ 10^{-4}\,T.$

(Assuming $C = 1{\cdot}808$; $\beta_r = 300.$)

In the case of tungsten the approximate thermodynamic formula (column IV.) so far as it can be derived from the specific heat measurements of Worthing, does not agree well with the experimental results, which are expressed quite as well linearly as by the Hertz formula employed by Langmuir. It is clear that vapour pressure measurements alone are generally insufficient for the determination of λ_0 without accurate knowledge of the variation of specific heats with temperature.

Since the change of specific heat of a supercooled liquid is not known precisely, the thermodynamic equation for the vapour pressure of a liquid

$$\ln p_T{}^l = -\frac{\lambda_0{}^s}{RT} - \left[\frac{l_m}{R} - \int_0^{T_m} \frac{C_p{}^s dT}{R} - \int_0^{T_m} \frac{C_p{}^l dT}{R}\right] \frac{T - T_m}{T_m}$$

$$+ \frac{C_p{}^g}{R} \ln T - \int_{T_m}^{T} \frac{dT}{RT^2} \int_{T_m}^{T} C_p{}^l dT - \int_0^{T_m} \frac{dT}{RT^2} \int_0^{T_m} C_p{}^s dT + C$$

cannot readily be evaluated. In order to obtain the true value of $\lambda_0{}^s$ and C, the vapour pressure has usually to be extrapolated to the melting point, and in the case of the molten elements it is generally sufficient to extrapolate by means of a linear equation.

The following linear equations are found to hold as closely as any three-constant formulæ in the following cases :—

Zinc: $\log p = -\frac{6170}{T} + 8{\cdot}107$

(*cf.* Braune's Measurements, *Zeit. Anorg. Chem.* cxi. p. 109, 1920).

Lead: $\log p = -\frac{10265}{T} + 8{\cdot}3165$

(*cf.* Ingold's Measurements, J. C. S. cxxi. p. 2419, 1922).

$\log p = -\frac{9923}{T} + 7{\cdot}908$ or $\frac{10350}{T} + 8{\cdot}347$

(Egerton, Proc. Roy. Soc. ciii. p. 469, 1923).

Cæsium: $\log p = -\frac{3753}{T} + 7{\cdot}256$

(Scott, Phil. Mag. xlvii. p. 32, 1924).

Rubidium: $\log p = -\frac{4269}{T} + 7{\cdot}331$ (*Ibid.*).

In the case of mercury, the linear relation

$$\log p = -\frac{3252{\cdot}2}{T} + 8{\cdot}1691$$

accords well with the measurements of Knudsen, and

$$\log p = -\frac{3117{\cdot}5}{T} + 7{\cdot}8300$$

with those of Smith and Menzies; it has already been pointed out (Phil. Mag. xxxix. p. 1, 1920) that the two careful sets of measurements do not agree well with each other, and experiments are being made to find out where the discrepancy lies.

The equations

$$\log p = -\frac{B'}{T} + A' \text{ or } \log p = -\frac{B}{T} - C\log T + A''$$

$$\text{or } \log p = -\frac{\lambda_0}{RT} + A'' + C''T$$

(where C and C'' have nearly the same values for all elements), lead necessarily to the Ramsay and Young equation

$$\frac{T_1'}{T_2'} = \frac{T_1}{T_2} + K(T_1' - T_1),$$

where K in the case of the 1st equation would be given by

$$\frac{A_2' - A_1'}{B_2'}R$$

(T_1 and T_2 are the temperatures of equal vapour pressure for two different substances).

Ingold (J. C. S. cxxi. p. 2419, 1922) has claimed for molten lead that the Ramsay–Young equation gives closer agreement than is obtained by extrapolation of the four-constant Nernst equations. Since the formulæ above cited (particularly the last) are very close approximations to the thermodynamic formula, the Ramsay and Young equation naturally should hold. Having fixed the vapour pressure of a certain metal, that of other metals can be found if one point on the vapour pressure line is fixed by careful measurement and consequently with some approximation λ_0 and the other thermal constants which enter into the thermodynamic vapour pressure formula.

Summary.

1. On the basis of the thermodynamic vapour pressure formula a linear equation $\log p = -\frac{a}{T} + b$ closely represents the variation of vapour pressure with temperature of a solid with monatomic vapour.

2. Various examples are given of the application of this equation.

3. A vapour pressure determination at a single temperature should suffice to determine the course of the whole curve.

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CI. *The Thermal Conductivity of Solid Electric Insulators.* —II. *By* W. M. Thornton, *Professor of Electrical Engineering, Armstrong College, Newcastle-upon-Tyne* *.

1. In a review of Debye's theory of the atomic heats of solids Jeans remarks †:—"Debye's result may be summarised in the statement that the whole heat-energy of an element resides in the energy of its elastic-solid vibrations, the atoms being treated as particles of the solid, and each vibration having exactly the energy allotted to it by the quantum-theory." It follows that the continuous transmission of heat through insulating solids proceeds in the same way.

For many electrical insulators the thermal conductivity k is proportional to the product of the longitudinal elasticity E and

* Communicated by the Author.

† Report on Radiation and the Quantum-Theory by J. H. Jeans, 2nd ed. §61, p. 60.

the density ρ, and $k = E\rho . 10^{-14}$ for widely different substances*. The rate of transmission of the elastic vibrations which constitute heat in solids is then proportional to the force between molecules of which elasticity is a measure. According to Nernst, Debye's formula for molecular heat takes account of the vibrations of the molecules, Einstein's of the atoms. The above relation supports this to the extent that for k to be proportional to E one of them must deal with molecular forces, and Einstein's professedly does not.

Expressing the heat k in mechanical units as $\frac{mv^2}{J}$, v is the difference of the mean square velocities of vibration between opposite sides of unit cube across which unit temperature gradient is maintained. The mass is numerically the density of the substance, so that $k = E\rho = \rho v^2/J$. The velocity of molecular heat vibration therefore follows the same law as that of sound, in that v^2 varies as the elasticity in the direction of transmission. This is the meaning of the relation between k, E, and ρ, given in the previous paper, which should therefore be true for all substances in which heat is transmitted by vibration of molecules, or of atoms when the energy of the latter bears a constant ratio to the former, as it does at normal temperatures.

2. In the case of graphite, $E = 5{\cdot}2 . 10^{11}$, $v^2 = EJ . 10^{-14}$, and $v = 460$ centimetres a second, increase of molecular velocity per degree rise of temperature. The average velocity for simple harmonic vibrations is 0·9 the root mean square value, and is 4 times the product of frequency and amplitude. At temperatures approaching the infra-red, with atomic frequencies about 10^{12}, the corresponding change of amplitude is in the case of graphite 10^{-10} centimetre, less than a hundredth of a molecular diameter, per degree, a not improbable value for atomic vibrations.

Molecular movement in solids at speeds equivalent to a frequency of the order of 10^{13} occurs in the passage of sound. When the molecules in the wave-front are all in phase the motion is transmitted as sound ; when they are in complete confusion, as heat, the elastic movement being the same in both cases.

3. Variations from the relation $k = E\rho$ have been pointed out by Clarke † in the case of certain glasses. The values

* "The Thermal Conductivity of Solid Insulators," Phil. Mag. xxxviii. p. 705, Dec. 1919.

† "The Thermal Conductivity of some Insulators," J. R. Clarke, Phil. Mag. xl. p. 502 (1920).

of k, calculated from observed elastic constants and densities, are in some cases higher, in others lower than if the relation were independent of composition. In the light of modern knowledge of molecular structure, glasses are complex interlaced lattices. The elasticity of the whole is not a known function of the forces within the molecule. When the thermal conductivity calculated from $E\rho$ is less than the observed value it may be accepted as an indication that the solid as a whole has less elasticity than its elements, or that the atomic vibrations which undoubtedly add to molecular heat, and are not so far as we know directly related to the elasticity E, retard by absorption the transmission of energy. When, on the other hand, the observed value of k is greater than E the interlocked lattices form a structure stiffer than the transmitted heat vibrations indicate.

Optical glasses are not, as Clarke states, very suitable for testing the validity of the relationship $k=E\rho$, though the agreement is in some cases close. Their composition is usually much more complex than that of the other insulators considered. Taking the Jena glasses 19 to 38 discussed by him, eleven have a thermal conductivity greater than $E\rho$, five have less. For all these the ratio $\frac{\Sigma(k)\text{ obs.}}{\Sigma(E\rho)}=1{\cdot}3$. The longitudinal elasticity is on the whole less than that by which heat movement is transmitted.

CII. *The Principle of Equivalence in the Theory of Relativity.* *By* Tracy Yerkes Thomas, *National Research Fellow in Mathematical Physics, Department of Physics, University of Chicago* *.

1. *Introduction.*

In considering the propagation of light in a gravitational field in 1911, Einstein † made the assumption that a homogeneous gravitational field is completely equivalent to a uniform acceleration of the coordinate system. This assumption is Einstein's *original* principle of equivalence. As thus stated, however, the principle applies only to the case of a homogeneous gravitational field, and is consequently unsuited for the requirements of the general theory of relativity.

* Communicated by the Author.

† A. Einstein, "Ueber den Einfluss der Schwerkraft auf die Ausbreitung des Lichtes," *Ann. d. Physik*, xxxv. p. 898 (1911).

Accordingly, in his formulation of the general theory of relativity in 1916, Einstein * replaced the above statement of the principle of equivalence by the assumption that the special theory of relativity holds in an infinitely small four-dimensional region for a proper choice of coordinates. This modification of his original assumption has retained the name of the principle of equivalence. The proper choice of coordinates is considered to be one for which the linear element or interval has the same form as in the special theory of relativity for some point in the infinitely small four-dimensional region. Beyond this, no definite specification of coordinates is made. This statement of the principle of equivalence furnishes a means by which we may pass from the laws of the special theory of relativity to those of the general theory. The principle suggests that the laws of the special theory of relativity when expressed in a form which is invariant under arbitrary transformations of coordinates will retain this form for the general theory of relativity. But, as has been pointed out by Eddington †, this method of generalization from a flat to a curved manifold cannot always be expected to lead to correct results. For if the general law depends on terms involving the curvature of the world, these terms will not be determined by such a method of generalization, since the curvature tensor vanishes identically in the special theory of relativity.

In this paper we give a statement of the principle of equivalence by means of *point-inertial* systems of coordinates. These systems are very closely related to the ordinary inertial systems of the special theory of relativity, and reduce to the latter in case the gravitational field can be removed by a transformation of coordinates. Point-inertial systems appear to be the "proper choice of coordinates" mentioned by Einstein in his later statement of the principle of equivalence. Their use gives a *unique* determination of the general laws from those of the special theory of relativity.

We assume the Riemann geometry as specified by the condition (2.3). It should be observed, however, that our statement of the principle of equivalence does not depend on the condition (2.3), but only on the existence of a fundamental metric tensor $g_{\alpha\beta}$ satisfying (5.2). This raises the question if it is not possible to apply the principle of equi-

* A. Einstein, "Die Grundlagen der allgemeinen Relativitätstheorie," *Ann. d. Physik*, vol. xlix. p. 769 (1916).

† A. S. Eddington, 'The Mathematical Theory of Relativity,' p. 40 (1923).

valence to this more general metric geometry, on the basis of which Einstein * has recently considered a new insertion of electricity in the theory of relativity. But such an application of the principle of equivalence has not been attempted in the present article.

2. *Riemann Geometry.*

We consider a system of paths,

$$x^i = \psi^i(s), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.1)$$

which take the place of the straight lines of euclidean geometry, and which are given as solutions of the set of differential equations † :

$$\frac{d^2x^i}{ds^2} + \Gamma^i_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds} = 0. \quad . \quad . \quad . \quad . \quad (2.2)$$

The Γ's in these equations are Christoffel symbols with respect to a symmetric tensor $g_{\alpha\beta}$; *i. e.*,

$$g_{\alpha\beta,\,\gamma} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.3)$$

where $g_{\alpha\beta,\,\gamma}$ denotes the covariant derivative of $g_{\alpha\beta}$. Under an arbitrary analytic transformation of coordinates,

$$x^i = g^i(\bar{x}), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.4)$$

which may also be written

$$\bar{x}^i = f^i(x), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.5)$$

the differential equations (2.2) of the paths (2.1) become

$$\frac{d^2\bar{x}^i}{ds^2} + \bar{\Gamma}^i_{\alpha\beta}\frac{d\bar{x}^\alpha}{ds}\frac{d\bar{x}^\beta}{ds} = 0. \quad . \quad . \quad . \quad . \quad (2.6)$$

It follows from (2.3) that the Γ's are Christoffel symbols with respect to the tensor $\bar{g}_{\alpha\beta}$, into which the tensor $g_{\alpha\beta}$ is transformed by the transformation (2.4).

It can be shown that (2.3) is a sufficient condition for the paths (2.1) to possess the homogeneous quadratic first integral

$$g_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds} = \mu^2, \quad . \quad . \quad . \quad . \quad . \quad (2.7)$$

where μ^2 is a constant for any particular path.

* *Cf.* the series of notes by A. Einstein in the *Berlin Sitzungsberichte* (1923).

† L. P. Eisenhart and O. Veblen, 'The Riemann Geometry and its Generalization,' Proc. Nat. Acad. Sci. vol. viii. p. 19 (1922).

We define the length l of a curve c extending between the points (x_0) and (x_1) by

$$l = \int_{x_0}^{x_1} \sqrt{g_{\alpha\beta} \frac{dx^\alpha}{dt} \frac{dx^\beta}{dt}}\, dt, \quad . \quad . \quad . \quad . \quad (2.8)$$

where t is the parameter occurring in the parametric representation of the curve c. In case the curve c is a path (2.1), the length l becomes

$$l = \int_{x_0}^{x_1} \mu\, ds = \mu(s_1 - s_0). \quad . \quad . \quad . \quad . \quad (2.9)$$

It follows from (2.8) that the linear element dl is given by:

$$dl^2 = g_{\alpha\beta} dx^\alpha dx^\beta. \quad . \quad . \quad . \quad . \quad . \quad (2.10)$$

The paths of zero length, which are light tracks in the theory of relativity, correspond to $\mu = 0$. Paths which are not of zero length are geodesics—*i. e.*, they are the curves for which the integral

$$\int_{x_0}^{x_1} \sqrt{g_{\alpha\beta} \frac{dx^\alpha}{dt} \frac{dx^\beta}{dt}}\, dt \quad . \quad . \quad . \quad . \quad (2.11)$$

is stationary.

3. *Normal Coordinates* *.

A unique solution (2.1) of the differential equations (2.2) is determined by a set of initial conditions:

$$x^i = p^i \text{ when } s = 0, \quad . \quad . \quad . \quad . \quad (3.1)$$

$$\frac{dx^i}{ds} = \xi^i \text{ when } s = 0. \quad . \quad . \quad . \quad . \quad (3.2)$$

This solution is of the particular form

$$x^i = p^i + \Gamma^i(p, \xi s). \quad . \quad . \quad . \quad . \quad . \quad (3.3)$$

Let us now put

$$y^i = \xi^i s. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.4)$$

Then the equations (3.3) become

$$x^i = p^i + \Gamma^i(p, y), \quad . \quad . \quad . \quad . \quad . \quad (3.5)$$

and these equations determine a transformation from the coordinates (x) to a new set of coordinates (y). The (y) coordinates defined by (3.5) are called *normal coordinates.*

* O. Veblen, "Normal Coordinates for the Geometry of Paths," Proc. Nat. Acad. Sci. vol. viii. p. 192 (1922).

A path (2.1) satisfying the initial conditions (3.1) and (3.2) is given by (3·4) in normal coordinates. Hence, if the functions $\Gamma^i_{\alpha\beta}$ are denoted by $C^i_{\alpha\beta}$ when transformed to a system of normal coordinates (y), the C's satisfy the condition

$$(C^i_{\alpha\beta})_0 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.6)$$

at the origin of normal coordinates.

It can be shown that under an arbitrary transformation of the (x) coordinates the normal coordinates (y) which are defined by the (x) coordinates and a point p suffer a linear homogeneous transformation with constant coefficients *. We may therefore determine a system of normal coordinates (y) at the origin of which (2.10) has the form

$$dl^2 = a_\alpha dy^{\alpha}{}^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.7)$$

where the a's are either ± 1. In case the a's are all $+1$, these normal coordinates are determined to within an orthogonal transformation.

4. *Extension of Tensors* †.

Let us denote by $T^{lm\ldots n}_{ij\ldots k}$ an arbitrary tensor which is contravariant in the indices $(l, m, \ldots, n)$ and covariant in the indices $(i, j, \ldots, k)$. Let us then define a set of functions $T^{lm\ldots n}_{ij\ldots k,\, p\ldots q}$ of (x) by

$$T^{lm\ldots n}_{ij\ldots k,\, p\ldots q} = \left(\frac{\partial^n T^{lm\ldots n}_{ij\ldots k}}{\partial y^p \ldots \partial y^q}\right)_0, \quad . \quad . \quad . \quad . \quad (4.1)$$

where the derivative is evaluated at the origin of a system of normal coordinates (y). It can be shown that $T^{lm\ldots n}_{ij\ldots k,\, p\ldots q}$ is a tensor which is contravariant in the indices $(l, m, \ldots, n)$ and covariant in the indices $(i, j, \ldots, k, p, \ldots, q)$. We shall call this tensor the nth extension of $T^{lm\ldots n}_{ij\ldots k}$, provided that there are n indices $(p, \ldots, q)$.

The first extension of any tensor is the ordinary covariant derivative of the tensor. However, the second extension of a tensor is not the same as the ordinary second covariant derivative of the tensor, and in general the nth extension $(n>1)$ is not the same as the ordinary nth covariant derivative of the tensor. Lists of formulæ of extension, together with formulæ giving the relations between various extensions, are given in the 'Geometry of Paths' (*loc. cit.*).

* O. Veblen and T. Y. Thomas, "The Geometry of Paths," Trans. Am. Math. Soc. vol. xxv. p. 551 (1923).

† O. Veblen and T. Y. Thomas, *loc. cit.*

For example, the second extensions of the covariant vector T_i and the covariant tensor T_{ij} are :

$$T_{i,\,pq} = \frac{\partial}{\partial x^p}\frac{^2T_i}{\partial x^q} - \frac{\partial T_i}{dx^a}\Gamma^a_{pq} - \frac{\partial T_a}{\partial x^p}\Gamma^a_{iq} - \frac{\partial T_a}{\partial x^q}\Gamma^a_{ip} - T_a\Gamma^a_{ipq}, \quad . \quad . \quad (4.2)$$

$$T_{ij,\,pq} = \frac{\partial^2 T_{ij}}{\partial x^p \partial x^q} - \frac{\partial T_{ij}}{dx^a}\Gamma^a_{pq} - \frac{\partial T_{aj}}{\partial x^p}\Gamma^a_{iq} - \frac{\partial T_{ia}}{\partial x^p}\Gamma^a_{jq} - \frac{\partial T_{aj}}{\partial x^q}\Gamma^a_{ip}$$

$$- \frac{\partial T_{ia}}{\partial x^q}\Gamma^a_{jp} - T_{aj}\Gamma^a_{ipq} - T_{ia}\Gamma^a_{jpq} + T_{a\beta}\Gamma^a_{ip}\Gamma^\beta_{jq} + T_{a\beta}\Gamma^a_{iq}\Gamma^\beta_{jp},$$

in which . . . (4.3)

$$\Gamma^i_{jkl} = \frac{1}{3}\left(\frac{\partial \Gamma^i_{jk}}{\partial x^l} + \frac{\partial \Gamma^i_{kl}}{\partial x^j} + \frac{\partial \Gamma^i_{lj}}{\partial x^k} - 2\Gamma^i_{aj}\Gamma^a_{kl} - 2\Gamma^i_{ak}\Gamma^a_{lj} - 2\Gamma^i_{al}\Gamma^a_{jk}\right). \quad (4.4)$$

The second extensions $T_{i,\,pq}$ and $T_{ij,\,pq}$ are related to the second covariant derivatives $T_{i,\,p,\,q}$ and $T_{ij,\,p,\,q}$ respectively by the formulæ :

$$T_{i,\,p,\,q} = T_{i,\,pq} - T_a A^a_{ipq}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.5)$$

$$T_{ij,\,p,\,q} = T_{ij,\,pq} - T_{aj}A^a_{ipq} - T_{ia}A^a_{jpq}, \quad . \quad . \quad (4.6)$$

where the A's are normal tensors.

5. *Point-inertial Systems.*

The special theory of relativity deals with a particular class of coordinate systems called inertial systems. These systems are characterized by the fact that the interval dl has the particular form,

$$dl^2 = dt^2 - dx^2 - dy^2 - dz^2, \quad . \quad . \quad . \quad . \quad (5.1)$$

where t denotes the time and (x, y, z) are the coordinates of a rectangular coordinate system. All inertial systems having their origins at a common point are related by a linear homogeneous transformation of the variables with constant coefficients called the Lorentz transformation, which possesses the property that it leaves the form (5.1) invariant. The invariance of (5.1) under the Lorentz transformation expresses the fact that a light-ray has a constant velocity (which we here take to be unity) in all inertial systems.

We make the assumption in the general theory of relativity that the metric is such that the a's in (3.7) have the values $a_0 = 1$, $a_1 = a_2 = a_3 = -1$. Hence 3.7 becomes

$$dl^2 = dy^{0\,2} - dy^{1\,2} - dy^{2\,2} - dy^{3\,2}. \quad . \quad . \quad . \quad . \quad (5.2)$$

The system of normal coordinates (y^0, y^1, y^2, y^3) at the origin

of which (5.2) holds is determined to within a Lorentz transformation.

We shall call the system of normal coordinates (y^0, y^1, y^2, y^3) a *point-inertial* system, on account of the similarity between these systems and the ordinary inertial systems of the special theory of relativity *. If there exists a transformation changing (2.10) into the form (5.2), this will be accomplished by the transformations leading to the point-inertial system, so that in such a case the form (5.2) will hold throughout the point-inertial system.

For convenience we shall also denote by (t, x, y, z) the coordinates of a point-inertial system. In this case the form (5.1) will hold at the origin of the point-inertial system.

The following properties of point-inertial systems relating these systems to the inertial systems of the special theory of relativity may readily be verified.

In the special theory :—	In the general theory :—
(1) The interval dl has the form (5.1) *throughout* the inertial system.	(1) The interval dl has the form (5.1) *at the origin* of the point-inertial system.
(2) The functions $\Gamma^i_{\alpha\beta}$ vanish *throughout* the inertial system.	(2) The functions $\Gamma^i_{\alpha\beta}$ vanish *at the origin* of the point-inertial system †.
(3) Light is propagated with the velocity unity *throughout* and relatively to all inertial systems.	(3) Light is propagated with the velocity unity *at the origin* of and relatively to all point-inertial systems.
(4) The covariant derivative is equal to the ordinary partial derivative *throughout* the inertial system. In general the nth extension is equal to the nth partial derivative *throughout* the inertial system.	(4) The covariant derivative is equal to the ordinary partial derivative *at the origin* of the point - inertial system. In general the nth extension is equal to the nth partial derivative *at the origin* of the point-inertial system.
(5) The equations of a path passing through the origin of the inertial system are of the form (3.4).	(5) The equations of a path passing through the origin of the point-inertial system are of the form (3.4).
(6) Inertial systems having their origins at a common point are related by the homogeneous Lorentz transformation.	(6) Point - inertial systems having their origins at a common point are related by the homogeneous Lorentz transformation.

* *Cf.* G. N. Birkhoff, 'Relativity and Modern Physics,' p. 118, § 7 (1923).

† It follows from the condition (2·3) that the first derivatives of $g_{\alpha\beta}$ vanish at the origin of the point-inertial system.

This comparison clearly shows that the point-inertial systems of the general theory of relativity are very closely related to the inertial systems of the special theory.

6. *Principle of Equivalence.*

The results of the preceding section suggest that the special theory of relativity will hold for an observer at the origin of the point-inertial system—*i. e.*, that the measurements of such an observer will have the significance of measurements of space and time in the special theory of relativity. We are thus led to consider that some of the laws (invariant equations) of the general theory of relativity will have the exact form of the corresponding laws of the special theory of relativity when referred to the origin of the point-inertial system. This assumption will be spoken of as the principle of equivalence. It will not be possible for every law of the general theory of relativity to assume the form of the corresponding law in the special theory at the origin of the point-inertial theory, as this would involve inconsistencies in the general laws. However, to every law of the special theory of relativity there will be a law of the general theory, which will be uniquely determined from the law of the special theory by means of the principle of equivalence.

The remaining sections of this paper will be devoted to particular applications of the principle of equivalence.

7. *Propagation of a Potential.*

The wave equation

$$\frac{\partial^2\phi}{\partial t^2}-\frac{\partial^2\phi}{\partial x^2}-\frac{\partial^2\phi}{\partial y^2}-\frac{\partial^2\phi}{\partial z^2}=0 \quad . \quad . \quad . \quad . \quad (7.1)$$

expresses the fact that the potential ϕ is propagated with the velocity of light unity. According to the principle of equivalence, this equation is to be introduced into the general theory of relativity by requiring that it be satisfied at the origin of the point-inertial system. As is customary, we denote by $g^{\alpha\beta}$ the cofactor of the corresponding $g_{\alpha\beta}$ in the determinant

$$g = \begin{vmatrix} g_{11}, \cdots, g_{14} \\ \\ g_{41}, \cdots, g_{44} \end{vmatrix}, \quad . \quad . \quad . \quad . \quad (7.2)$$

divided by the determinant g. Then $g^{\alpha\beta}$ constitutes a contravariant symmetric tensor, and the equation (7.1)

which holds at the origin of the point-inertial system can be written in the invariant form

$$g_{\alpha\beta}\phi_{,\,\alpha\beta} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.3)$$

where $\phi_{,\,\alpha\beta}$ is the second extension of the potential ϕ*.

Let us denote by $\square$ the operation of forming the second extension of a scalar, vector, or tensor, and then contracting the indices of extension by multiplication with $g^{\alpha\beta}$. Thus, in general,

$$\square T^{lm\ldots n}_{ij\ldots k} = g^{\alpha\beta} T^{lm\ldots n}_{ij\ldots k,\,\alpha\beta}, \quad . \quad . \quad . \quad . \quad (7.4)$$

where $T^{lm\ldots n}_{ij\ldots k,\,\alpha\beta}$ is the second extension of the tensor $T^{lm\ldots n}_{ij\ldots k}$.

The equation (7.3) may now be written

$$\square\phi = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.5)$$

Hence, according to the principle of equivalence, the wave equation (7.1) takes the form (7.5) when introduced into the general theory of relativity.

8. *Conservative Equations.*

According to the principle of equivalence, the laws of conservation of energy and momentum will hold in the ordinary sense for the observer at the origin of the point-inertial system. This assumption has its expression in the equations

$$\frac{\partial \mathfrak{T}^{\mu}_{\nu}}{\partial y^{\mu}} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.1)$$

referred to the origin of the point-inertial system, where $\mathfrak{T}^{\mu}_{\nu} = \sqrt{-g}\,T^{\mu}_{\nu}$ is the tensor density of the energy tensor T^{μ}_{ν} and depends on the energy density of the electromagnetic field and ponderable matter. On account of the condition (2.3), the equations (8.1) become

$$\frac{\partial T^{\mu}_{\nu}}{\partial y^{\mu}} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.2)$$

also referred to the origin of the point-inertial system. We do not know the exact form of the tensor T^{μ}_{ν} inside the elementary electrical charges, but a form which is sufficiently accurate for many purposes is given by

$$T^{\mu}_{\nu} = \rho g_{\nu\sigma}\,\xi^{\sigma}\,\xi^{\mu}, \quad . \quad . \quad . \quad . \quad . \quad (8.3)$$

* The second extension and the second covariant derivative of a scalar function ϕ are identical.

where ρ denotes the stationary density of matter and ξ^σ is a vector which is equal to $\frac{dx^\sigma}{ds}$ along any world-line. Inserting (8.3) into the conservation equations (8.2), we obtain well-known equations of hydrodynamics *.

Transforming the equations (8.1) to arbitrary coordinates, we obtain

$$\frac{\partial \mathcal{J}^\mu_\nu}{\partial x^\mu} - \Gamma^\sigma_{\nu\tau} \mathcal{J}^\tau_\sigma = 0. \quad . \quad . \quad . \quad . \quad . \quad (8.4)$$

Hence, according to the principle of equivalence the equations (8.4) express the laws of conservation in the general theory of relativity.

9. *Gravitational Equations.*

We assume that the gravitational potentials $g_{\mu\nu}$ are propagated with the velocity of light in the ordinary galilean sense for the observer at the origin of the point-inertial system. We meet this requirement by putting

$$\Box g_{\mu\nu} = \psi_{\mu\nu}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.1)$$

where $\psi_{\mu\nu}$ is a symmetric "tensor of matter" which, like the energy tensor T^μ_ν, may be assumed to depend on the energy density of the electromagnetic field and ponderable matter. For at the origin of the point-inertial system (9.1) becomes

$$\frac{\partial^2 g_{\mu\nu}}{\partial t^2} - \frac{\partial^2 g_{\mu\nu}}{\partial x^2} - \frac{\partial^2 g_{\mu\nu}}{\partial y^2} - \frac{\partial^2 g_{\mu\nu}}{\partial z^2} = \psi_{\mu\nu}, \quad . \quad . \quad . \quad (9.2)$$

and the ordinary solution of an equation of this form involving retarded potentials will therefore apply at the origin of the point-inertial system. Hence the observer at the origin of the point-inertial system will consider that the gravitational potentials $g_{\mu\nu}$ are propagated with the velocity of light unity †.

If space were euclidean, then the Γ's would vanish throughout the point-inertial system. In reality space is not euclidean, although its actual deviation from the euclidean is very slight; we therefore assume that space is euclidean

* *Cf.* A. S. Eddington, *loc. cit.* p. 117.

† A similar treatment may evidently be given for electromagnetic waves. This would lead to equations of the form $\Box \phi_{\mu\nu} = \theta_{\mu\nu}$, where $\phi_{\mu\nu}$ is the skew-symmetric electromagnetic tensor and $\theta_{\mu\nu}$ is a skew-symmetric tensor of matter.

to the extent that the Γ's and their first derivatives are negligibly small in the point-inertial system. The g's will differ but slightly from the galilean values in the point-inertial system, and the gravitational equations (9.1) will therefore take the form (9.2) very approximately throughout this system. We thus arrive at an approximate theory of gravitational waves very similar to that given by Einstein *. But the principle of equivalence gives an exact theory of the propagation of gravitational waves. For, according to this principle, the gravitational equations (9.1) express the fact that the gravitational potentials $g_{\mu\nu}$ are propagated with the velocity of light for the observer at the origin of the point-inertial system, the only place where we can speak of a velocity of propagation in the ordinary sense.

We obtain the Einstein gravitational equations from (9.1) if we assume that these equations contain the equations of conservation (8.2). This assumption may be satisfied by putting

$$\psi_{\mu\nu} = k(\mathrm{T}_{\mu\nu} - \tfrac{1}{2} g_{\mu\nu}\mathrm{T}), \quad . \quad . \quad . \quad . \quad (9.3)$$

in which

$$\mathrm{T}_{\mu\nu} = g_{\mu\sigma}\mathrm{T}^{\sigma}_{\nu},$$

$$\mathrm{T} = g^{\mu\nu}\mathrm{T}_{\mu\nu},$$

and k is a constant. By the substitution (9.3), we have

$$\Box g_{\mu\nu} = k(\mathrm{T}_{\mu\nu} - \tfrac{1}{2} g_{\mu\nu}\mathrm{T}). \quad . \quad . \quad . \quad . \quad (9.4)$$

To prove that the equations (9.4) yield the conservation equations (8.2), we shall transform these equations into the ordinary Einstein equations of the gravitational field, namely ;

$$\mathrm{R}_{\mu\nu} - \tfrac{1}{2} g_{\mu\nu}\mathrm{R} = -\kappa \mathrm{T}_{\mu\nu}, \quad . \quad . \quad . \quad . \quad . \quad (9.5)$$

where k is a constant, and

$$\mathrm{R}_{\mu\nu} = \mathrm{B}^{\sigma}_{\mu\sigma\nu},$$

$$\mathrm{R} = g^{\mu\nu}\mathrm{R}_{\mu\nu},$$

the tensor B being the curvature tensor. We first write the equations (2.3) in the form

$$\frac{\partial g_{\mu\nu}}{\partial x^{\alpha}} = g_{\sigma\nu}\Gamma^{\sigma}_{\mu\alpha} + g_{\mu\sigma}\Gamma^{\sigma}_{\nu\alpha}. \quad . \quad . \quad . \quad . \quad (9.6)$$

If we transform these equations to a normal coordinate system, differentiate, and evaluate at the origin of the

* A. Einstein, "Ueber Gravitationswellen," *Berlin Sitzungsberichte*, p. 154 (1918).

normal coordinates, we obtain

$$g_{\mu\nu,\,\alpha\beta} = g_{\sigma\nu}\mathrm{A}^{\sigma}_{\mu\alpha\beta} + g_{\mu\sigma}\mathrm{A}^{\sigma}_{\nu\alpha\beta}, \quad . \quad . \quad . \quad (9.7)$$

whose $g_{\mu\nu,\,\alpha\beta}$ is the second extension of the fundamental metric tensor $g_{\mu\nu}$ and the A's are normal tensors. Now the normal tensor $\mathrm{A}^{\sigma}_{\mu\alpha\beta}$ and the curvature tensor $\mathrm{B}^{\sigma}_{\mu\alpha\beta}$ satisfy the equations

$$3\mathrm{A}^{\sigma}_{\mu\alpha\beta} = \mathrm{B}^{\sigma}_{\mu\alpha\beta} + \mathrm{B}^{\sigma}_{\alpha\mu\beta} \quad . \quad . \quad . \quad . \quad . \quad (9.8)$$

identically. Using this identity, we may show that

$$3g_{\mu\nu,\,\alpha\beta} = g_{\alpha\sigma}(\mathrm{B}^{\sigma}_{\mu\beta\nu} + \mathrm{B}^{\sigma}_{\nu\beta\mu}) . \quad . \quad . \quad . \quad (9.9)$$

Hence *

$$\Box g_{\mu\nu} = \tfrac{2}{3}\mathrm{R}_{\mu\nu} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.10)$$

By means of the identity (9.10) we easily transform the equations (9.4) into the Einstein equations (9.5). Hence the equations (9.4) contain the conservation equations (8.2), since it is well known that the divergence of the left member of (9.5) vanishes identically.

10. *Motion of a Mass Particle.*

The differential equations of motion of a freely-moving mass particle in the special theory of relativity are

$$\frac{d^2y^i}{ds^2} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10.1)$$

where y^0 denotes the time and (y^1, y^2, y^3) are the coordinates of a rectangular coordinate system. These equations, when referred to the origin of the point-inertial system, are the differential equations of a path (2.1). Hence, according to the principle of equivalence, the track of a freely-moving mass particle in the general theory of relativity is a path (2.1). The equations of motion of the freely-moving mass particle which pass through the origin of the point-inertial system will therefore be

$$y^i = \xi^i s, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10.2)$$

where the ξ's are constants. Hence to the observer at the origin of the point-inertial system the particle will appear to move in a euclidean straight line. But the particle will not in general appear to move in a euclidean straight line if it does not pass through the origin of the point-inertial system.

* The second extension $g_{\mu\nu,\,\alpha\beta}$ is identical with a tensor $\phi_{\mu\nu,\,\alpha\beta}$ defined by Birkhoff, who also obtains equations which are essentially the same as (9.10). *Cf.* G. N. Birkhoff, *loc. cit.* pp. 123 and 229.

11. *Track of a Light Ray.*

In the special theory of relativity the track of a light ray satisfies the differential equations (10.1) and also the condition that along it the constant $\mu=0$. Hence, according to the principle of equivalence, the track of a light ray in the general theory of relativity is a path (2.1) of zero length. As in the case of the mass particle, the observer at the origin of the point-inertial system will consider the track of the light ray which passes through the origin to be a euclidean straight line; but in general this will not be the case if the track does not pass through the origin.

A path (2.1) is uniquely determined by a set of initial conditions (3.1) and (3.2). Hence, if we assume that the track of a light ray is a path (2.1), it should be possible to determine this path by imposing the initial condition that at a remote point where the metric may be assumed to be galilean the ray has the velocity of light c in the ordinary sense, *i. e.*

$$\left(\frac{dx^1}{dx^0}\right)^2+\left(\frac{dx^2}{dx^0}\right)^2+\left(\frac{dx^3}{dx^0}\right)^2=c^2, \quad . \quad . \quad . \quad (11.1)$$

where x_0 denotes the time and (x^1, x^2, x^3) are rectangular coordinates.

The problem of showing that such a determination of the light path would be identical with the determination given by the condition that the path be of zero length was proposed to me by Professor Swann. The solution of this problem is immediate, for if we introduce the parameter s in (11.1) this equation becomes

$$c^2\left(\frac{dx^0}{ds}\right)^2-\left(\frac{dx^1}{ds}\right)^2-\left(\frac{dx^2}{ds}\right)^2-\left(\frac{dx^3}{ds}\right)^2=0 \quad . \quad (11.2)$$

or

$$g_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds}=0, \quad . \quad . \quad . \quad . \quad . \quad (11.3)$$

where the g's have galilean values. But (11.3) must be satisfied at all points of the light path, since it is satisfied initially. Hence $\mu=0$ for the light path, and the path is of zero length. Conversely, if the light track is a path of zero length and the g's may be assumed to have galilean values at some remote point, then the ray has the velocity of light c in the galilean sense at this point.

We should notice that in the solution of this problem we have made explicit use of the condition $\mu=0$ for a path of zero length.

CIII. *An Effect of Argon on the First Positive Band Spectrum of Nitrogen.* *By* R. C. Johnson, *B.A., Ph.D., Lecturer in Physics, Queen's University, Belfast* *.

[Plate XXVI.]

THE first positive band spectrum of Nitrogen is peculiar in the extent to which it may be modified under various conditions of excitation. It was shown in 1911 by Strutt and Fowler † that one such modification of the system constituted part of the spectrum of the nitrogen afterglow. This consisted in a special development of some three of the more refrangible flutings in each band group, or, more precisely, the luminous energy was found to be concentrated in three only of the thirteen series which normally express the complete radiation of the system. Thus, the series developed are obtained by putting

$$\begin{cases} m = 47 & \text{and} \quad p = 42, 43, 44, \\ m = 46 & \text{and} \quad p = 41, 42, 43, 44, \\ m = 45 & \text{and} \quad p = 40, 41, 42, 43, \end{cases}$$

in $$\nu = 22785{\cdot}1 - \frac{30{\cdot}319}{8}(2m)^2 + \frac{29{\cdot}363}{8}(2p+1)^2.$$

Further modification of the system has been described by Rayleigh ‡, when the afterglow is produced from mixtures of nitrogen with the inert gases helium, argon, and neon. The most remarkable feature (which was studied in some detail in the case of helium) is a pronounced shift of spectral intensity towards the less refrangible end as the percentage of the inert gas in the mixture is increased. Under these circumstances the selective action of the afterglow conditions, together with the energy displacement induced by the inert gas, render the first positive band spectrum of nitrogen almost unrecognizable.

More recently, variations induced by the inert gases in the fine structure of the second positive bands of nitrogen have been described by Steubing and Toussaint §, but no mention is made by them of similar variations in the first positive bands.

While working with tubes containing argon imperfectly

* Communicated by Prof. W. B. Morton, M.A.

† Proc. Roy. Soc. A, lxxxv. p. 377 (1911), and later papers.

‡ Proc. Roy. Soc. A, cii. p. 453 (1923).

§ *Zeitschr. f. Phys.* Jan. 1924, p. 128.

purified—*i. e.*, mixed with a trace of nitrogen—we have noticed the appearance of the band spectrum in a considerably modified form. The effect is similar to that in the afterglow, and consists in the development of a few only of the band heads of each group. The selection is most pronounced with a trace of nitrogen in high-pressure argon. With increasing percentage of nitrogen the selection of bands which become visible increases almost symmetrically, the normal development of the spectrum being restored for percentages greater than about five.

This selective action of argon on the first positive band spectrum, though similar in character, is to be distinguished in origin from the selective effect found in the nitrogen afterglow. In the experimental work, we used wide-bore glass discharge-tubes containing the mixed gases at a total pressure of 10 mm. and excited by an ordinary uncondensed discharge. Under these circumstances the afterglow was not visible unless the percentage of nitrogen was considerable (say greater than 20). Even if it be suggested that at lower percentages the nitrogen afterglow might have been present though not sufficiently intense for visual observation, it is clear that this could not account for an effect which is *most* pronounced with the *lowest* percentages of nitrogen (when the supposed afterglow would be least strong). Further, Rayleigh * observed that in the production of the afterglow (using a *condensed* discharge) in mixtures of nitrogen and argon, the glow became too faint for observation for percentages of nitrogen less than 25.

These facts finally dispose of any possibility of an afterglow origin for the selective effect which we have described.

The modified band spectrum has been further investigated by us, and a systematic search was made for an induced energy displacement in the several band groups. A series of tubes containing variously accurately known percentage mixtures of nitrogen and argon were photographed through a neutral wedge † mounted in front of the slit of a prism spectroscope. In this way negatives were obtained showing the intensity distribution in the band system. Pl. XXVI. shows a few typical photographs. Spectra 4 and 5 are respectively of pure nitrogen

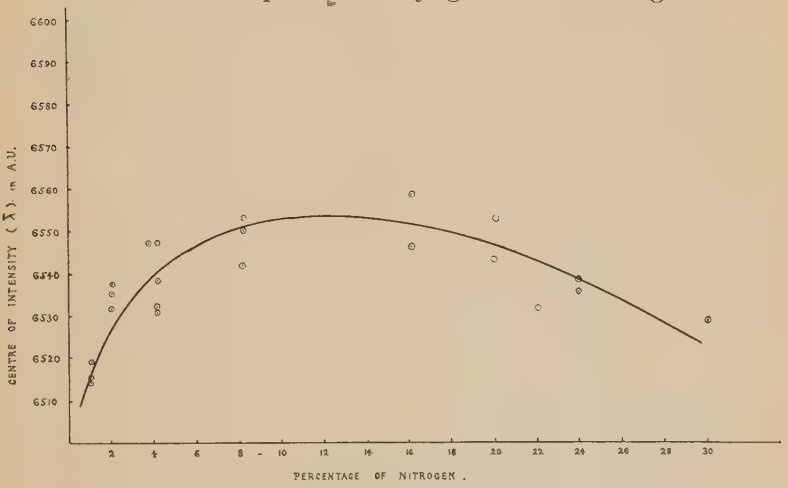
* *Loc. cit.*

† For the theory of the neutral wedge, see papers by Merton and Nicholson: Phil. Trans. A, ccxvi. p. 459, and ccxvii. p. 239.

at low pressure, and of a trace of nitrogen in 10 mm. of argon. The latter shows the selective effect strongly. Spectra 1 and 2 are, from this point of view, over-exposed. By successive photographic reproduction of the negatives, plates were obtained having sufficiently sharp contrast to permit of micrometric measurement. The height of the band heads in each group was measured, and these were converted into photographic intensities by the formula

$$I = \log_{10}^{-1}(d_\lambda h),$$

where d_λ is the optical density gradient of the gradient



of the wedge for a wave-length λ, and h is the height of the band head. By forming the quantity

$$\bar{\lambda} = \frac{\Sigma I\lambda}{\Sigma I}$$

for each band group, we obtain a wave-length which may be described as the "optical centre of gravity," or, better, the "centre of intensity" of the group. Attention was confined to the red group, and the large quantity of data accumulated is disposed in the graph of "Centre of Intensity" against "Percentage of Nitrogen." It will be observed that the range of experimental error seems rather wide. This, however, is difficult to avoid, as it arises from

(1) Errors in $\bar{\lambda}$ due to inaccuracy in measurement of h, owing to irradiation etc., and

(2) Variation from the initial percentage due to appreciable disappearance of nitrogen in the discharge.

The results, however, are sufficient to indicate that for traces of nitrogen in argon there is an energy displacement of some 30 to 40 Å.U. towards the more refrangible end. This, indeed, is the analogue of the selection of three of the *more refrangible* flutings of the red group in the afterglow spectrum. Both phenomena are illustrated in the graph, the downward course of the curve for higher percentages being interpreted as due to the appreciable formation of active nitrogen.

Discussion.

According to Fowler and Strutt*, the afterglow is produced during the re-formation of molecular nitrogen from atomic or so-called "active" nitrogen. The electrical conditions within the afterglow must therefore be the result of the inter-atomic electric fields. In the enlarged state of the activated molecules these fields naturally have effects on neighbouring or interposed atoms and molecules of another kind, which will as a consequence have their spectra excited. In this connexion an application of Klein and Rosseland's theory of inelastic collisions of the second type has recently been made by Saha and Sur †. They have shown that the excitation of other spectra in the afterglow is in every case explained by a "radiationless transfer" of energy from the active nitrogen molecules to the particular molecules introduced. This may take place to the extent of the total energy with which the activated molecules are loaded, viz. about 8·5 volts. No attempt, however, is made by these investigators to explain that peculiar selection of the first positive bands of nitrogen which constitute the visible spectrum of the afterglow. It seems at first sight attractive to assume that it originates in radiationless transfer from the activated to the inactive molecules, which latter must be present in large excess. As a consequence we should expect initial nuclear orbits of small quantum number to preponderate. Taking the red band group, by way of illustration, we find, for example ‡, the transitions giving the afterglow are from initial quantum orbits $p=40$, 41, 42 to final orbits $m=45$, 46, 47 ; while $p=43$, 44, 45, and 46, which usually occur strongly in the first positive band system, are absent. On the other hand, orbits $p=38$ and 39, which usually occur faintly, are not present at all in the afterglow, while the above theory suggests that they would be strengthened.

* *Loc. cit.*

† Phil. Mag. (6) xlviii. p. 421 (1924).

‡ See table in Phil. Mag. (6) iii. p. 348 (1902).

We now proceed to discuss the consequences of the experimental work described in the present paper.

The effect of argon which we have described would seem to be quite in harmony with the view advanced tentatively elsewhere *, that the electrical conditions obtaining in the afterglow are of a similar character to those found when an uncondensed discharge is passed through high pressure argon. It is reasonable to assume that at any given time the activated molecules will only constitute a very small fraction of the total number, so that the greater part will be ordinary nitrogen molecules, and in this inactive state must bear the relation of a comparatively high-pressure inert gas towards those which are radiating. The similarity which experiment appears to suggest is therefore between molecules radiating, on the one hand, in a virtually inert atmosphere (of un-ionized nitrogen molecules) where only inter-atomic fields due to the activated molecules exist, and, on the other hand, in an inert atmosphere of a foreign gas to which external electric fields are applied. It may be reasonably contended that under *ordinary discharge conditions* the radiating molecules will only constitute a very small fraction of the total number present, which suggests at first sight that the above similarity should hold in every case. The fundamental difference, however, between ordinary discharge conditions and those of the afterglow is that in the former external electric fields are applied, while in the latter case there are no fields except such as might arise from the activated molecules themselves. In the afterglow the excess of un-ionized molecules breaks up any fields that might exist between the activated ones, so that the latter radiate in the more or less complete absence of electrical fields. This we believe to be the clue to the structure of the afterglow spectrum. In high-pressure argon we probably have an approximation to these conditions. Here, in order to produce the radiation, an external field is applied; but the excess of argon atoms, which themselves produce no radiation and are therefore closed systems, operate so as to break up strong electric fields, in this way shielding the radiating nitrogen molecules from all those which are other than of the mildest character.

From this point of view the afterglow selection might be regarded as the "normal" radiation of this molecule, and the more familiar first positive band spectrum a result of the influence of electrical fields on the radiation. This does not furnish by any means a complete explanation, but as a working hypothesis it explains the similarity which

* Proc. Roy. Soc. A, cvi. p. 200 (1924).

experiment has indicated, and it may be of service in elucidating the reasons for structural modifications induced in spectra excited in the afterglow. It would follow from the analogy that, just as the selective action on the nitrogen bands is most pronounced with only a trace of nitrogen present in argon, so the afterglow selection should be most pronounced the instant before the glow dies away—that is to say, the light from an end-on stream of nitrogen in which the afterglow is dying away would yield an intensity distribution which is but the integral of a varying one. According to our theory, this distribution is a function of the percentage of active molecules present, so that the range of the integration would be from this initial value to zero. A critical test would therefore be found in a comparison of the intensity distribution in the first positive bands photographed in the afterglow at various points down the stream. (These would require, of course, very different times of exposure.)

It seems quite possible that all the various modifications produced in spectra excited by the nitrogen afterglow may be reproduced in high-pressure argon, and this matter is also receiving further investigation.

I wish to take the opportunity of thanking Mr. W. H. B. Cameron and Miss M. E. Hall for their valuable assistance.

Abstract.

Traces of nitrogen in high-pressure argon show the first positive band spectrum in a considerably modified form. This consists in a selection of a few only of the band heads of the various groups, and the general effect is similar to that found in the afterglow spectrum. Quantitative investigations are described which indicate that there is an energy displacement towards the more refrangible end of each band group. This also is similar to the conditions of the afterglow. It is suggested that all the phenomena hitherto regarded as peculiar to the electrical conditions obtaining in the afterglow may be reproduced in high-pressure argon. The bearing of these facts on the nature of the afterglow spectrum is discussed.

DESCRIPTION OF PLATE XXVI.

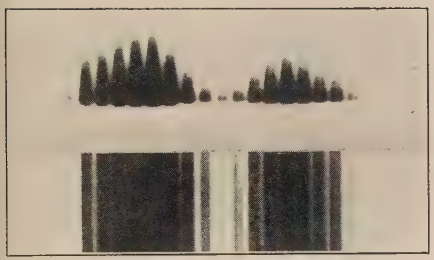
No. 1. Spectrum and wedge photograph of argon-nitrogen mixture containing less than 1 per cent. of nitrogen.

No. 2. Argon-nitrogen mixture containing 2 per cent. nitrogen.

No. 3. Argon-nitrogen mixture containing 12 per cent. nitrogen.

No. 4. Pure nitrogen at low pressure. Wide-bore tube. Uncondensed discharge.

No. 5. Spectrum photograph showing the selective effect of argon on the nitrogen band spectrum. Taken from a tube containing a trace of nitrogen in argon at 10 mm. pressure.



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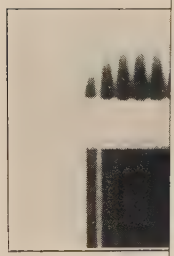

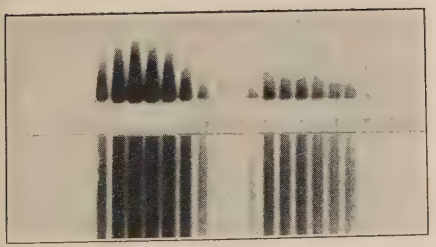

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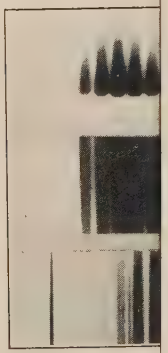


CIV. *The Decay of Radium E.*

By L. Bastings, *B.A.*, *M.Sc.* (*N.Z.*) *.

Introduction.

THE β-ray emission of radium E has long been of considerable interest. Schmidt † first showed that the β rays are resolved in a transverse magnetic field into a continuous spectrum, in which have since been detected no spectral lines such as are produced with all other β-ray bodies except UrX. This spectrum from RaE indicates a continuous distribution of velocity in the rays emitted, from very small velocities up to, according to Danysz ‡, velocities in the neighbourhood of $2{\cdot}8 \times 10^{-10}$ cm. per sec. At the same time, the amount of γ radiation is extremely small, its ionizing power having been variously estimated by Schmidt § and by Meyer and Schweidler ‖ at from ·016 to ·033 per cent. of that due to the β rays. This small ratio is in marked contrast to that for all other β-ray substances: *e.g.*, for RaC the ratio is approximately 100 per cent., for ThD 74 per cent., and even for UrX 2 per cent.

It is now generally considered probable that the β rays comprising a line-spectrum are ejected from extranuclear orbits by the action of γ rays proceeding from the nucleus, and owe their varied velocities to their originating from different energy-levels of the atom. But in the case of RaE, as with other continuous β-ray spectra, all the β rays probably have their origin in the nucleus itself, and it is not easy to see how such great differences in velocity can arise in the disintegration of nuclei presumably all alike. Now, one important respect in which the atoms are assumed to be alike is implied in the exponential law of decay—viz., that all the atoms present have the same probability of decay, irrespective of any attendant circumstances. But a conceivable explanation of the heterogeneity of the rays might be found in the assumption that the atoms do not all possess exactly the same probability of decay; that, for example, the atoms evolving fast β rays might disintegrate at a more rapid rate than those ejecting slow particles, and in consequence possess a decay constant differing from the average constant, as deduced from the usual decay measurements. Now the faster β particles can easily be separated from the rest by interposing a

* Communicated by Sir E. Rutherford, F.R.S.

† *Phys. Zeit.* viii. p. 361 (1907).

‡ *Le Radium*, x. p. 4 (1913).

§ *Loc. cit.*

‖ *Wien. Ber.* cxv. p. 119 (1906).

suitable thickness of metal foil; and if there is any difference in the average life of the atoms in the way suggested, the ionization produced by the faster particles should die away more rapidly than that revealed by the heterogeneous beam from the bare source. Such a theory of the continuous spectra can best be tested by means of RaE, since the problem is not complicated by the presence of any homogeneous β rays, or any appreciable γ radiation.

Further interest is added to the case of RaE by the fact that widely differing values of the half-period have been obtained, while at one time it was even believed by some that RaE consisted of two distinct bodies of periods as widely apart as 4·8 and 6·2 days. The following is a summary of the results on record for the half-period :—

Rutherford	(1)	4·5 days
,, ...	(2)	6 ,,
Giesel	(3)	6 ,,
Meyer & Schweidler	(4)	4·8 & 6·2 ,,
Antonoff	(5)	5 ,,
Thaller	(6)	4·85 ,,

(1) Phil. Trans. A, cciv. p. 169 (1905); Phil. Mag. viii. p. 636 (1904).
(2) Phil. Mag. x. p. 290 (1905).
(3) *Ber. d. D. Chem. Ges.* xxxix. p. 780 (1906).
(4) *Wien. Ber.* cxvi. p. 701 (1907).
(5) Phil. Mag. xix. p. 825 (1910).
(6) *Wien. Ber.* cxxi. p. 1611 (1912).

Experimental Procedure.

The RaE sources were prepared by dissolving in dilute HCl the equilibrium products contained in old emanation tubes, and electrolyzing out the E on to platinum electrodes with a current density of about 2×10^{-4} amps. per sq. cm. The deposit was then dissolved off in dilute HCl, and a clean nickel disk rotated in the warm solution for from a half to two hours. With some of the smaller sources, the electrolytic process was omitted. This procedure resulted in fairly pure RaE, the amount of RaD obtained producing a residual activity which in only one case exceeded $\frac{1}{2}$ per cent. of the initial activity of the source, and in most cases was considerably less than this. (The percentage residues for the various sources were: ·08, ·03, ·14, ·002, ·61, ·22, ·05, ·008.) In every case these residual effects were carefully measured some weeks afterwards, and due allowance made by subtracting the value for the residue from the values obtained throughout the decay.

Comparison was made between a bare source of weak intensity and a stronger source covered with a suitable

thickness of aluminium, up to 1·1 mm., in which case the intensity of the ionization is reduced to less than 1 per cent. of its original value. Also both sources were deposited on equal-sized disks of the same metal, this precaution being perhaps of importance in view of the evidence recently adduced by Mlle St. Maracineanu* of the slow diffusion of radioactive sources into metals on which they are deposited.

Three different methods of attacking the problem were successively attempted :—

(*a*) A direct estimate of the apparent decay constant of the sources was made by measuring the ionization produced by each, at regular intervals, for a period of up to 20 days. The measurements were made in the usual way with a β ray electroscope, with the leaf insulated by a sulphur bead inside the ionization chamber. The electroscope was standardized regularly with a constant β-ray source—viz., an old emanation tube in equilibrium, in which the controlling factor RaD, having a half-period of about 17 years, would vary by only 0·23 per cent. in 20 days. The constancy of the natural leak was checked at frequent intervals.

Further reference will be made to these measurements later. They revealed no difference of the kind sought to an accuracy of 1 per cent.

(*b*) In the next method, two sources were initially adjusted as before to give identical ionization at the same instant, and an attempt was made to measure any subsequent possible difference in the ionization produced by them. Two exactly similar ionization cans were constructed, and their insulated electrodes connected together to one pair of quadrants of a Dolezalek electrometer, used heterostatically. The walls of the ionization chambers were connected to a suitable high voltage, one being maintained positive and the other negative. Any initial difference, such as that due to unequal natural leak, was taken up by a subsidiary ionization can of smaller dimensions, suitably arranged. The decay of the sources was followed for about 20 days ; but a limit to the accuracy was imposed by the large capacity of the system in relation to the comparatively small sources available. No further information on the problem was added to that obtained in (*a*) ; and the method proved more difficult and less reliable.

(*c*) A third method proved much more successful. The sources, adjusted to approximate equality, as before, were measured alternately by the β-ray electroscope of method (*a*). By making a large number of comparisons at frequent

* *C. R.* clxxvii. p. 1215 (1923).

intervals over a period of several hours, and discarding all but highly concordant results (due allowance being made for decay), values can be obtained for the ratio between the sources, from which have been eliminated any sensible errors due to variations in the action of the electroscope. Such average ratios were obtained at least twice daily for about three weeks.

Results.

The results of this last method are best revealed by tabulating, in their order, the ratios obtained, the values in each column corresponding to measurements spread over five consecutive days.

	1·138	1·137	1·140	1·144
	1·140	1·134	1·143	1·144
	1·144	1·140	1·144	1·139
	1·137	1·141	1·145	1·140
	1·136	1·137	1·143	1·145
	1·142	1·138	1·139	1·135
	1·139	1·144	1·143	1·139
	1·139	1·141	1·136	1·136
	1·146	1·137	1·139	1·135
	1·134	1·141	1·139	1·137
				1·141
Means	$1·395_5$	$1·139_0$	$1·141_1$	$1·139_6$
Average	$1·139_6$			
Mean deviation from average .	$·002_8$	$·002_3$	$·002_6$	$·003_0$

Maximum deviation from average ..... $·006_4$
Mean „ „ ..... $·002_7$

A real change in the ratio from 1·139 to 1·141 in 5 days would correspond to a difference in decay constant of 0·3 per cent. between those atoms evolving fast particles and the average atom. These results therefore point conclusively to the absence of any systematic difference in the average life of the two classes of atoms. We are therefore still without any adequate explanation of the homogeneity of the β rays in the continuous spectrum of this or other β-ray products.

It may also be remarked that the above results indicate that a β-ray electroscope, when used under the most favourable circumstances, may be relied on to about 1 in 500.

The Decay Constant.

The value for the half-period usually accepted is 4·85 days, as deduced by Thaller * by averaging 16 results (varying from 4·6 to 5·0) of measurements made by him in the usual way.

In connexion with the measurements of this constant undertaken under method (*a*) above, it was soon realized

* *Wien. Ber.* cxxi. p. 1611 (1912).

that Thaller's value is too low. So further measurements of the constant were made with several fresh sources in the manner previously indicated. In all, seven sources have been followed for from 20 to 30 days ; and in every case the residual activity, due to RaD contamination, has been estimated after 50 days or more, and due correction applied. The most probable value of the constant in each case, and its probable error, were deduced from the data by the method of least squares ; while to the various values of the activity of each source, weights were attached, varying in magnitude with the activity of the source. The average result was also arrived at by attaching weights in accordance with the above probable errors.

The results are summarized in the accompanying table.

Source.	Period, in days.	Probable error.	Weight attached.
A	5·04	±·04	1
B	4·96	±·03	1
C	5·02	±·04	1
D	5·02	±·02	2
E	4·98	±·02	2
F	4·97	±·01	3
G	4·96	±·01	3
Weighted mean.....		$t = 4{\cdot}98_5$ days $\pm{\cdot}00_4$	
Corresponding decay constant...		$\lambda = 0{\cdot}139_0$ day^{-1}	

Table of Decay.

As this constant differs by about 3 per cent. from that adopted for tables of decay published for RaE *, it may be

Hours.	Activity.	Days.	Activity.	Days.	Activity.
0	1·0000	0	1·0000	17	·0941
0·5	·9971	1	·8704	18	·0819
1	·9942	2	·7572	19	·0713
2	·9885	3	·6592	20	·0620
3	·9827	4	·5734	25	·0310
4	·9771	5	·4990	30	·0155
5	·9714	6	·4343	35	·0077
6	·9658	7	·3780	40	·0038
7	·9602	8	·3290	45	·0019
8	·9542	9	·2862	50	·0010
9	·9491	10	·2491	60	·0002
10	·9436	11	·2168	66	·0001
11	·9381	12	·1886		
12	·9328	13	·1642		
15	·9168	14	·1426		
18	·9011	15	·1243		
21	·8854	16	·1082		

* *E. g.* Meyer and Schweidler, *Radioactivität*, 1916, p. 365.

of value to add such a table, based on the above value of the constant, and calculated by the aid of Newman's Table of Exponentials *.

SUMMARY.

(1) No appreciable difference has been detected between the decay constant of those radium E atoms ejecting fast β particles and the average radium E atom.

(2) A value of the decay constant of radium E,

$$\lambda = 0{\cdot}139_0 \pm {\cdot}000_1 \text{ day}^{-1},$$

has been obtained, corresponding to a half-period of $4{\cdot}98_5$ days.

I have much pleasure in recording my gratitude to Professor Sir Ernest Rutherford for suggesting the problem, and for his helpful interest during its prosecution; also to Dr. J. Chadwick for criticism and help, especially in the preparation of the unusually large RaE sources required.

The Cavendish Laboratory,
Cambridge,
July 28, 1924.

CV. *The Apparent Value of Poisson's Ratio for Beams of Varying Cross-Section.* *By* H. WRIGHT BAKER, *M.Sc., A.M.I.M.E., Lecturer in Engineering at the University of Manchester* †.

WHEN a beam is subjected to a uniform bending moment, curvature occurs in a plane containing the longitudinal axis of the beam and also in transverse planes perpendicular to this axis. Assuming the simple theory of bending to be applicable, it can be shown that the ratio of the two radii of curvature has the same value as Poisson's ratio for the material of the beam. Early experimental determinations of Poisson's ratio for metals by the method of flexures were made by Mallock (Proc. Roy. Soc. xxix. 1879). Four small wire pillars were attached to the surface of the beam, in the planes of bending, so that on loading the beam the free ends of a pair of pillars either approached each other or receded according to the direction of curvature. By measuring these relative movements with the aid of a microscope, and knowing the length of the pillars and the distance apart of their bases, the radii of curvature of the beam were found.

* Trans. Camb. Phil. Soc. xiii. p. 145 (1883).

† Communicated by the Author.

The method was further improved by Carrington (Phil. Mag. [6] xli. p. 206, 1921), who fastened small mirrors to the pillars and determined their relative angular movements by measuring the deflexions produced on beams of light after successive reflexion from the two mirrors of each pair.

Guided by the sensitiveness of the methods of measurement employed, these investigators have used beams capable of considerable flexure, the breadth : depth ratio chosen being 4 and 5·7. Experiments by the author, while approximately confirming the results for thin beams obtained by Carrington, lead him to doubt the constancy of the values for a given material but with varying cross-sections. Tests have therefore been made on a series of beams for which the ratio of breadth to depth varied from 3·7 to 0·27.

When experimenting on narrow beams, the small deflexions and the shortness of the base available for the measurement of anticlastic curvature prevent the use of Carrington's method in its simple form and without the employment of elaborate means of preventing vibration.

The system of measurement to be described virtually consists in replacing Carrington's mirrors by pieces of plate glass, adjusting these to be approximately parallel and almost in contact, and measuring the spacing, perpendicular to the beam, of the interference bands seen when monochromatic light is reflected from the two inner surfaces.

If the plates are secured to the sides of a beam of breadth "b," and "n" is the change, produced by bending, in the number of bands between two gauge lines at a distance "l" apart, then "θ," the angle of inclination of the sides of the beam, is given by $n \times \frac{1}{2}$ (wave-length of light)$/l$, and the corresponding radius of anticlastic curvature is b/θ.

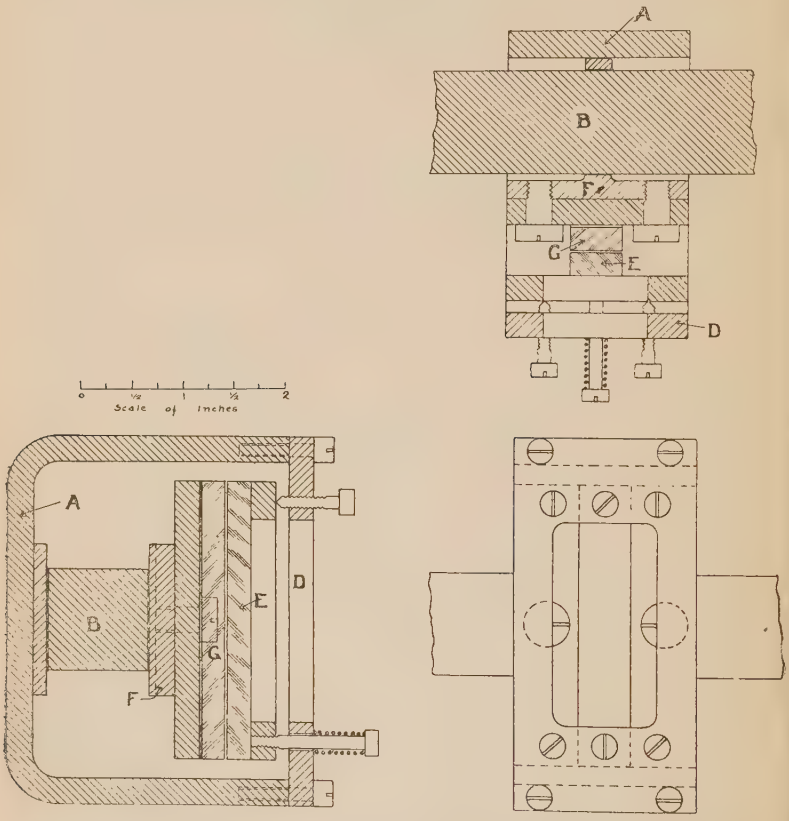
The glass plates, carried in adjustable brass frames, were at first clamped to the beam, but persistent "creep" occurred during the tests, both when using plane and 3-point contacts. A number of other methods have been tried, the most satisfactory being that of soldering the frames to the beam, using a solder having a melting-point of about 100° C.

Fig. 1 shows the final form of the interferometer.

The body A is soldered to one side of the beam B, a packing strip a quarter of an inch wide being interposed. In the front-plate D a rectangular window is cut, and behind this, held on an adjustable frame, is a stout strip of plate-glass E. A brass back-plate F is soldered to the opposite side of the beam (the breadth of contact again being $\frac{1}{4}$ in.), and carries the rear glass G. The rear reflecting surface is therefore controlled by the front side of the beam, and *vice versa*.

The chief advantages of this form of apparatus are its rigidity and ease of adjustment, and also the absence of any relative movement of the plates other than the angular movement to be measured, sharp definition of the interference bands being therefore maintained for all conditions of flexure. It is assumed that the sides of the beam, for a length of $\frac{1}{4}$ in. where the interferometer is attached, remain

Fig. 1.



plane during bending, and that the glass plates are subjected therefore to the movement of the whole depth of the beam. Though "creep" has not been entirely eliminated, its magnitude has been reduced to reasonable dimensions, and further improvements might be effected by the provision of hardened and polished contacts on the adjusting mechanism.

The plates are illuminated from a distance of 2 feet by a sodium flame about 4 inches high, produced by hanging a fine strand of asbestos soaked with brine in a suitable

bunsen flame. Care is required to obtain a uniform light for all conditions of bending.

For counting the "bands" between two gauge marks drawn in ink on one of the reflecting faces, a low-power telescope is used. This is mounted on the horizontal axis of a theodolite frame to enable the image of the cross-hair to be traversed slowly across the field as a pointer, thus greatly reducing eye-strain.

In the tests recorded in the present paper the beams were supported on knife edges 21 inches apart, one of these having been free to swing horizontally to prevent end constraint. A state of pure bending was produced by loads applied outside the supports, these having been increased in stages to a maximum corresponding to a skin stress of 10,000 lb./in.^{2} and then gradually reduced to zero. Longitudinal curvature was measured in the usual way with scale, mirror, and telescope, arranged on an optical base of 20 feet.

The tests cover the useful range of the interferometer for the deeper sections of beams, this being fixed almost entirely by the "creep." The change of zero-reading recorded has usually amounted to about one band, a comparatively small amount when dealing with shallow sections giving a total shift of 100 bands or more, but far outweighing all other sources of error for the deepest section used, for which a shift of only 11 bands was recorded. For very shallow sections a telescope of considerable power is required owing to the close spacing of the bands, and it is advisable to set the plates so that their relative inclination reverses at about half load. It has been customary to distribute the zero error equally between the curves of loading and unloading.

Preliminary tests on bright-rolled mild steel bars indicated a considerable variation in the apparent value of Poisson's ratio with change of section. The results, however, were not consistent, owing to a corresponding variation of the properties of the material due to rolling, affected to an unknown extent by the high temperature required to melt the tinsmith's solder which was then employed.

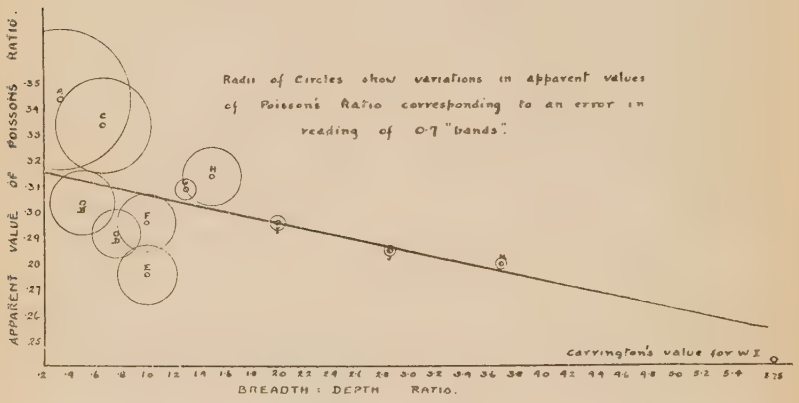
The curve shown in fig. 2 gives the results of 11 tests on "Armco" iron, the value obtained by Carrington for wrought iron being also added.

In addition to the distribution of the zero error as already indicated, small corrections have been made to the direct readings of longitudinal curvature. Within the limits of experimental error the radius of curvature has agreed with the simple theoretical value given by $\frac{\text{moment of inertia of section}}{\text{bending moment}} \times E$, where E is the modulus

of direct elasticity and is constant. The radius has therefore been re-calculated, assuming E to have the mean value obtained during the tests. In all cases the graphs of bending moment and radii of curvature have been straight lines.

With these corrections the greatest variation between the curve shown and the observation points is at E, and corresponds to an error of reading of two interference bands, the error at A and the mean error for the tests amounting to 0·8 band.

Fig. 2.


APPARENT VALUE OF POISSON'S RATIO.
Radii of Circles show variations in apparent values of Poisson's Ratio corresponding to an error in reading of 0·7 "bands".
Carrington's value for W I
BREADTH : DEPTH RATIO.

It would appear, therefore, that the apparent value of Poisson's ratio increases uniformly with the depth of section from about 0·26 for a breadth : depth ratio of 5·2 (Carrington's value ·245 for a ratio of 5·7) to ·315 for a ratio of 0·2, and is independent of the stress up to 10,000 lb./in.^{2}

It is interesting to compare the variations shown by this curve for iron with the results obtained by Cornu (*Comptes Rendus*, 1869) and Straubel (*Annalen der Chemie und der Physik*, lxxiii. p. 395) for small glass beams, the radii of curvature in these cases being measured by placing a plate of glass on the upper surface of the beam and examining the interference bands shown by monochromatic light. The first observer records a variation from ·227 for a breadth : depth ratio of 12 : 1 to a mean of ·246 for a ratio of 2·7, the latter giving a corresponding variation over a more restricted range of beams.

In conclusion the author would acknowledge his indebtedness to Messrs. A. Markwick, B.Sc., and W. L. D. Martyn, B.Sc., for much valuable assistance in the experimental work.

CVI. *Latent Heats of Fusion.*—Part II. *Palmitic Acid and Benzene.* *By* Mrs. K. Stratton, *M.Sc.*, *and* Professor J. R. Partington, *D.Sc.**

THE experiments described in the present paper form a continuation of those previously published†, but the apparatus has been slightly modified for convenience in working.

1. Palmitic Acid.

The Palmitic Acid used in the experiments was obtained originally from a specially pressed sample supplied by Price's Patent Candle Company. It was distilled twice at 100 mm. pressure, and the fraction coming over between 267° and 270° C. collected. This was recrystallized from petrol (B.Pt. 100°–110° C.); most of the acid was recrystallized at least twelve times.

After each recrystallization from petrol the product was dried in air, then put on a water-bath at 100°, and air drawn through it for about an hour to remove the last traces of petrol.

The recrystallizations were carried out with about ten different samples; the table below gives the results in two cases.

	1st Sample. Setting-Point.	2nd Sample. Setting-Point.
6th recrystallization.....	62·125° C.	62·15° C.
7th „	62·185° C.	62·165° C.
8th „	62·215° C.	62·20° C.
9th „	62·215° C.	62·225° C.
10th „	62·245° C.	62·24° C.
11th „	62·25° C.	62·25° C.
12th „	62·25° C.	62·25° C.

The Setting-Point of the mixture of Samples I. and II. was 62·25° C.

The Melting-Point of the mixture of Samples I. and II. was 62·65° C.

The melting-point was taken in the following way:—Finely powdered acid was placed in a test tube supported in a 500-c.c. beaker containing 300 c.c. of water, fitted with an efficient stirrer, and the thermometer was used for the stirrer in the acid. The heating of the bath was very gradual: about 45 minutes were required to warm the water from 16° C. to the temperature of melting.

The setting-points of the acid referred to above were determined in the usual form of apparatus: an inner tube,

* Communicated by the Authors.

† Phil. Mag. xliii. p. 436 (1922).

a strong test tube in this case, containing the powdered acid was supported by means of a cork in an air-jacket; the air-jacket was fixed in a water-bath, and the water in the bath heated and kept well stirred.

The acid in the inner tube was allowed to melt completely, then allowed to cool very slowly. As soon as the acid showed signs of setting, the bath was kept as nearly as possible at 62·5° C. with a very small flame and efficient stirring. The setting-point curves of pure specimens drawn from data of cooling experiments gave steady values at 62·25° C. The data previous recorded include the following:—

M.P. of Acid.	Beilstein, vol. ii. p. 370:	62·618° C.
	Landolt-Börnstein, p. 374:	62·618° C.
S.P. of Acid.	Landolt-Börnstein, p. 1430:	60° C.

Acid supplied by Kahlbaum, used in a previous research (Partington, Trans. Chem. Soc. xcix. p. 313, 1911), had a setting-point of 60° C.

The apparatus used in the previous experiments was modified to some extent. A stout cover for the whole apparatus, except for the inside beaker containing the acid, was made from sheet aluminium; the centre beaker was covered by a cork, as previously, cut so as to allow a space for the thermometer and heating-coil. The outermost enamelled iron vessel contained water at a temperature about 2° higher than that of the molten acid in the bath; the temperature of this water was kept fairly constant by placing the outer vessel in a large box packed with cotton-wool. The inside bath contained the pure acid in a molten condition and kept well stirred.

A weighed amount of the acid, well powdered, was placed in the innermost vessel, and the temperature gradually raised by being in contact with the bath of molten acid until a thermometer in the centre of it showed it to be at the setting-point 62·25° C. To ensure that the whole of the acid was at the setting-point, it was kept at this temperature for at least an hour before any heating by the coil was commenced.

The heating-coil in this case was of platinum wire joined to thick platinum leads. The wire was wound into a small coil of about $\frac{3}{4}$ inch length, and the windings kept in position by being fixed on to a small piece of glass rod. The rod bearing the coil was fused on to about 6 inches of glass rod, and this longer rod could then be used as a stirrer during the experiment. For purposes of connexion, the thick platinum leads were soldered on to leads of thick copper wire.

The quantity of electricity used in an experiment was estimated with a carefully regulated stop-clock and a calibrated ammeter, the latter reading to the second place of decimals. As confirmation of the readings of these two instruments, a copper coulometer was also used in some estimations.

Test experiments were performed with the ammeter, clock, and copper coulometer. The results of a typical experiment are given below :—

Weight of Copper deposited in coulometer = 0·5490 grm.
0·5490 grm. of Cu is equivalent to 0·5490/0·000328 = 1673·8 coulombs.

Ammeter reading = 1·55 amperes.
Time ,, = 18 mins. 2 secs.

1·55 amp. for 18 mins. 2 secs. is equivalent to 1677 coulombs. The difference is below 0·2 per cent.

Results of 4 *experiments*: using ammeter and clock.

Weight of Substance.	Current.	Time.	Value of L.
32·9625 grms.	1·53 amps.	35 mins. 48 secs.	51·24
30·8935 grms.	1·55 amps.	32 mins. 54 secs.	50·97
30·3970 grms.	1·54 amps.	32 mins. 30 secs.	51·27
31·1485 grms.	1·54 amps.	33 mins. 5 secs.	50·72

Experiment for check with Copper coulometer.

33·4880 grms. Acid.

Weight of Cu deposited in coulometer = 1·0758 grms.,
Ammeter reading = 1·55,

giving a value for L, the Latent Heat of Fusion, of 50·94.

The mean value of L from the five experiments is **51·03**.

The resistance of the platinum coil used in the experiments, corrected for the resistance of leads and for temperature, was 1·41 ohms.

The formula used for the calculation of L was, as before :

$$L = C^2Rt/4{\cdot}18\,W \text{ grm. cal. per gram.}$$

Determinations of the value of the Molecular Depression of the Freezing-Point of this same Palmitic Acid were made with a Beckman freezing-point apparatus. The solute used was Mesitylene (B.P. 162° C.).

Weight of Palmitic Acid.	Weight of Mesitylene.	Depression.	E.
12·5055 grms.	0·1980 grm.	0·57° C.	43·24
11·3749 grms.	0·1407 grm.	0·44° C.	42·75
12·6547 grms.	0·1471 grm.	0·42° C.	43·39

E = Depression of the Freezing-Point of Palmitic Acid on the addition of 1 grm. molecular weight of mesitylene to 100 grms. of the acid.

The calculation of the value of L, from the above values of E, by means of the formula

$$E = 0{\cdot}0198T^2/L,$$

gave the following results :

E = 43·24	L = 51·6
E = 42·75	L = 52·2
E = 43·39	L = 51·44

Landolt-Börnstein, p. 1430, give E=44.

As a check on the possibility of error owing to association of the mesitylene dissolved in the acid, determinations of the lowering of the freezing-point of pure Benzene were carried out in order to see how they compared with the recognized values of E for Benzene :—

Weight of Benzene.	Weight of Mesitylene.	Depression.	E.
15·3697 grms.	0·1416 grm.	0·39° C.	50·86
15·0893 grms.	0·1266 grm.	0·36° C.	51·52
16·1610 grms.	0·1941 grm.	0·518° C.	51·80

Landolt-Börnstein, p. 1427, give E=51·2 for Benzene.

These determinations of the value of E show that Mesitylene is not associated in Benzene solution, and therefore it probably is not associated in solution in Palmitic Acid.

The agreement between values of E determined from these two sets of experiments removes entirely the discrepancy of nearly 20 per cent. between found and calculated values for E given in Nernst's *Lehrbuch*, 1921, p. 158, and shows that Palmitic Acid shows quite normal behaviour in this connexion.

2. Benzene.

Determinations of the value of L for Benzene were also carried out in the same apparatus. The "Pure" Benzene of Kahlbaum was re-fluxed with a 25 per cent. aqueous solution of mercuric acetate, washed well with distilled water, dried with calcium chloride, re-fluxed with metallic sodium, and then fractionated. The product gave no test for thiophen with isatin, and had a boiling-point of 80·49° C. In the experiments a weighed amount of pure benzene was frozen before being put into the bath of molten benzene. It was allowed to stand in the bath until the thermometer in the centre of the solid benzene registered the same as that of the bath, 5·85° C., so that the setting-point of the Pure Benzene used was 5·85° C. Landolt-Börnstein (1912, p. 240) give B.P. 80·2°, M.P. 5·58°.

	Weight of Benzene.	Amperes.	Time.	Value of L.
(1)	49·8705 grms.	1·53 amp.	30 mins.	29·76
(2)	55·820 grms.	1·54 amp.	33 mins.	29·63
(3)	55·247 grms.	1·53 amp.	34 mins. 2 secs.	30·45
(4)	51·3906 grms.	1·56 amp.	31 mins. 58 secs.	29·83

Average value of L=29·92 grm. cal.
Landolt-Börnstein give L=30·11.

The resistance of the platinum coil used in these experiments was 1·479 ohms.

Summary.

The latent heats of fusion, and the molecular depressions of freezing-point (with mesitylene as solute), have been determined for carefully purified palmitic acid and benzene by the method described in a former communication.

	M.Pt.	S.Pt.	B.Pt.	L gm. cal. per gm.	E for 100 grm. solvent.
Palmitic acid ...	62·65° C.	62·25° C.	267–270/100 mm.	51·03	43·13
Benzene	.....	5·85° C.	80·49° C.	29·92	51·39

The results remove the large discrepancy between the observed and calculated values of E in the case of palmitic acid which are given in the literature.

The authors desire to express their thanks to the Chemical Society for a grant to one of them (K. S.), which largely covered the expense of the investigation, and to Price's Candle Co. for a specially expressed sample of Palmitic Acid which they very kindly supplied.

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CVII. *Some Problems of Two-dimensional Hydrodynamics.* *By* Dorothy M. Wrinch, *D.Sc., Lecturer at Lady Margaret Hall, Oxford* *.

THIS paper treats the motion of a cylinder in fluid when the curve of cross-section of the cylinder is a member of the series of curves given by the equations

$$x = a\cos u + \tfrac{1}{2}b\cos 2u$$

$$0 < b < a$$

$$y = b\sin u - \tfrac{1}{2}b\sin 2u.$$

These curves form an interesting set and range from the well-known star-like curve with three cusps (sometimes called the three-cusped hypocycloid) when b is equal to a,

* Communicated by the Author.

through the series of liqueur-bottle shapes as b decreases to $\frac{1}{2}a$ to tadpole-like curves when b decreases through smaller values to zero. This series has been selected for treatment because it comprises curves with concave and convex arcs

Fig. 1.

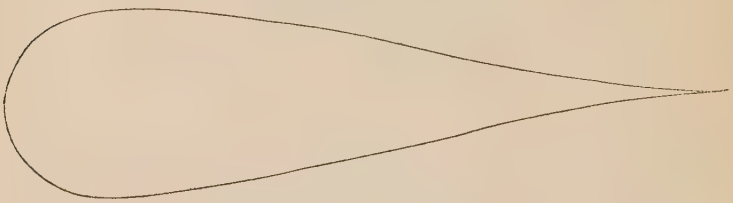


Fig. 2.

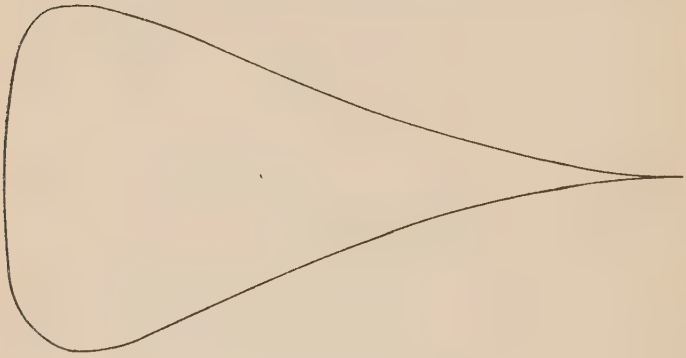


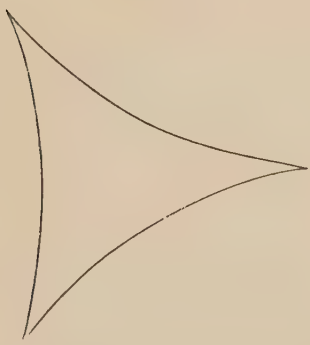
Fig. 3.

and cusps of a type not hitherto subjected to exact mathematical analysis. Further, the existence of the whole series of curves makes the results obtained of wide application; for many curves of a type resembling the liqueur-bottle type or the tadpole type can be treated at least approximately by interpolation between the curves of this series.

In this paper we work out a number of problems of classical hydrodynamics associated with a cylinder whose cross-section is of the specified type. Thus, we discuss first the motion of a fluid streaming past such a cylinder with a uniform velocity. Next we discuss the motion when the cylinder moves with uniform translational velocity in a fluid at rest at a great distance. Next we take the motion when the cylinder rotates with uniform angular velocity about its axis in a fluid at rest at a great distance. Next we discuss the motion when there is circulation of the fluid round the cylinder.

Fig. 4.

Fig. 5.



The development of aerodynamical research into the usefulness of wing profiles of various types in aerofoils of high aspect ratio, lends special interest to new results of the type we are here concerned with, especially in the case when the curve of cross-section has a cusp which constitutes the trailing edge of the wing. But it is well known that when the velocity in the neighbourhood of the wing becomes large at any point

classical hydrodynamics becomes quite inapplicable, and a new treatment which takes into account the viscosity of the air becomes imperative. Now, in accordance with the well-recognized theory of hydrodynamics, there is, in general, an infinite velocity at the cusp associated with each of the types of motion we have mentioned. But, it is not so well recognized that there exist in general combinations of any two of these three distinct types of motion which give a uniformly finite velocity at all points. The fact that it is possible to get a uniformly finite velocity in the case of a combination of translation and circulation has been noticed by Joukowsky *, and has led to the formation of his assumption now current in the Circulatory Theory of Lift in Aerodynamics †. For these reasons it has been deemed worth while to work out various combinations of the pure types, which have the characteristic that the velocity is everywhere finite, in addition to the pure types themselves. These mixed motions are evidently applicable to aerofoils of high aspect ratio when the various constants involved are so chosen that the velocity, now always finite, is sufficiently small.

1. *Description of the Curves.*

The equation of the curves of cross-section is taken in the form

$$x = x(u) = a\cos u + \tfrac{1}{2}b\cos 2u$$
$$y = y(u) = b\sin u - \tfrac{1}{2}b\sin 2u, \qquad 0 \leq b \leq a$$

in terms of the parameter u which increases uniformly from $-\pi$ to $+\pi$ on a complete description of the curves. The curves have one axis of symmetry, namely, the x-axis; but they are not symmetrical about the y-axis under any circumstances. We have

$$dx/du = -a\sin u - b\sin 2u,$$
$$dy/du = b\cos u - b\cos 2u,$$

and in consequence, if ψ is the angle made with the axis of x by the tangent to the curve at any point u,

$$\tan\psi = b(\cos u - \cos 2u)/\sin u(a + 2b\cos u).$$

* See N. Joukowsky, *Aérodynamique* (traduit du russe par S. Drzewiecki), Gauthier-Villars, Paris, 1916, chapter vi.

† See A. R. Low, "Circulation Theory of Lift," Report of the International Air Congress, London, 1923; also, "Hydrodynamics in its Application to Aeronautics," 'Dictionary of Applied Physics,' vol. v. p. 187 (1923).

Thus at the point $u=0$, ψ is π; and at the point $u=\pi$, $\psi=3\pi/2$. Whatever the value of the proper fraction b/a, there is a cusp at the point $u=0$, and there is a rounded base in the neighbourhood of the point $u=\pi$. Further, apart from the point $u=0$, a curve belonging to the series has its tangent parallel to the axis of x only at the points given by $\cos u=-\frac{1}{2}$, *i. e.* at the points $u=\pm 2\pi/3$. At these points $y=\pm 3\sqrt{3}\,b/4$ and $x=-\frac{1}{2}(a+\frac{1}{2}b)$. The maximum width of the curve is, in consequence, $3\sqrt{3}\,b/2$, and the curve attains this width at points at a distance $-\frac{1}{2}(a+\frac{1}{2}b)$ from the origin of coordinates, measured along its axis of symmetry, the x-axis. The curve cuts its axis of symmetry at $x=a+\frac{1}{2}b$ and at $x=-a+\frac{1}{2}b$; thus its major axis is of length $2a$. Apart from the points $u=\pm 2\pi/3$, the tangent to the curve is parallel to the y-axis only when

$$a+2b\cos u=0.$$

Thus, it is only when $\frac{1}{2}a<b<a$ that there any such points. As b ranges from $\frac{1}{2}a$ to a, these points range from $u=\pi$ when $b=\frac{1}{2}a$ to $u=\pm 2\pi/3$ when $b=a$. Further,

$$d^2x/du^2=-(a\cos u+2b\cos 2u),$$

$$d^2y/du^2=-b(\sin u-2\sin 2u).$$

Thus,

$$\begin{aligned}
f(u) &= dx/du\,.\,d^2y/du^2-dy/du\,.\,d^2x/du^2\\
&= b(a\cos u+2b\cos 2u)(\cos u-\cos 2u)\\
&\qquad +b(a\sin u+b\sin 2u)(\sin u-2\sin 2u)\\
&= b(a-2b+(2b-a)\cos 2u\cos u+(b-2a)\sin 2u\sin u)\\
&= b(a-2b+(b-\tfrac{1}{2}a)(\cos u+\cos 3u)\\
&\qquad +(\tfrac{1}{2}b-a)(\cos u-\cos 3u))\\
&= b(\tfrac{3}{2}(a-b)(1-\cos u)-\tfrac{1}{2}(a+b)(1-\cos 3u))\\
&= b(a+b)(k^2\sin^2 u/2-\sin^2 3u/2),
\end{aligned}$$

where

$$k=(3(a-b)/(a-b))^{\frac{1}{2}}.$$

Now, the curve is concave to the axis of x when $f(u)$ is positive, and convex when $f(u)$ is negative, and when $f(u)$ vanishes there is a point of zero curvature. Now, $f(u)\gtrless 0$ according as

$$|\sin 3u/2|\gtrless k\,|\sin u/2|.$$

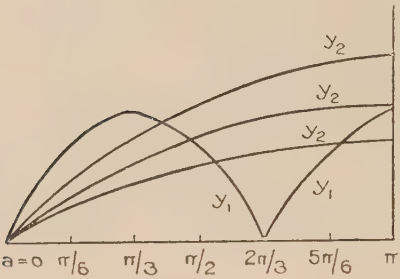
We give a diagram showing

$$y_1 = \sin 3u/2$$

and

$$y_2 = k \sin u/2,$$

Fig. 6.



y_2 being shown for various values of k, ranging from zero when a and b are equal through the value unity when $b = \frac{1}{2}a$, to the value $\sqrt{3}$ when b is zero. We need discuss only the cases when u is positive, since the curve is symmetric about the axis of x. It will be seen that whatever the value of k, $f(u)$ is negative from $u=0$ to a certain point $u=u_0$, which is less than $2\pi/3$, and is less remote from $2\pi/3$ as k increases. When k is less than unity, *i. e.* when b is less than $2a$, $f(u)$ is positive from u_0 to π. With the curves for which b is less than $\frac{1}{2}a$, we therefore have a convex arc from $u=0$ to $u=u_0$ and then a concave arc from $u=u_0$ to $u=\pi$: $u=u_0$ is, of course, a point of inflexion. If, however, b is greater than $\frac{1}{2}a$, in general there is still a convex arc from $u=0$ to $u=u_0 \leq 2\pi/3$, a point of inflexion at u_0 and then a concave arc; but in these cases the concave arc is terminated at a point u_1 lying between $2\pi/3$ and π, which is a point of inflexion, and the curve is then again convex to the point $u=\pi$. This alternation of convexity and concavity in the series of curves for which b is greater than $\frac{1}{2}a$ has interesting effects on the various solutions of hydrodynamical problems associated with cylinders with these curves as cross-sections with which we shall presently deal.

To find the values of u_0 and u_1, we put

$$\begin{aligned} f(u) &= b(a+b)(k^2 \sin^2 u/2 - \sin^2 3u/2) \\ &= b(a+b)\ (\sin^2 u/2 (k^2 - (4\cos^2 u/2 - 1)^2) \\ &= b(a+b) \sin^2 u/2 (k^2 - (2\cos u + 1)^2). \end{aligned}$$

Thus, $f(u)$ vanishes when $u=0, \pi$, and when

$$\cos u = -\tfrac{1}{2} \pm \tfrac{1}{2}k.$$

In consequence,

$$\cos u_0 = -\tfrac{1}{2}(1-k),$$
$$\cos u_1 = -\tfrac{1}{2}(1+k);$$

u_0 is evidently always real, since k ranges from zero to $\sqrt{3}$ only; u_1, on the other hand, only exists when k lies between zero and unity. We have, indeed, when $k=0$ and a and b are equal

$$u_0 = u_1 = 2\pi/3,$$

and when $k=1$ and $b=\frac{1}{2}a$

$$u_0 = \pi/2, \quad u_1 = \pi,$$

and when $k=\sqrt{3}$ and b is zero

$$u_0 = 68\tfrac{1}{2}^\circ.$$

It will be noticed that in the extreme case when $a=b$, $u_0=u_1$ and a cusp takes the place of the points of inflexion.

Diagrams of various members of the series of curves are given in figs. 1–5. The following values of the proper fraction b/a have been selected for illustration :—

$$2/10, \quad 2/5, \quad 2/4, \quad 2/3, \quad 2/2.$$

The extreme case when a and b are equal is the well-known hypocycloid with three cusps; the extreme case when b vanishes is the terminated straight line.

Streaming past a Cylinder.

Consider the W-function

$$W_0 = \phi_0 + i\psi_0$$

given by

$$W_0 = -q_0 z e^{-i\gamma},$$

so that

$$\phi_0 = -q_0(x\cos\gamma + y\sin\gamma),$$
$$\psi_0 = -q_0(y\cos\gamma - x\sin\gamma),$$

where ϕ_0 is the velocity potential and ψ_0 the stream function associated with some motion. Since

$$-\partial\phi_0/dx = q_0\cos\gamma,$$
$$-\partial\phi_0/dy = q_0\sin\gamma,$$

it evidently represents motion of fluid streaming with velocity q_0 in a direction making an angle γ with the axis of x.

Now suppose that a cylinder whose cross-section is the curve c whose equation is

$$x = a\cos u + \tfrac{1}{2}b\cos 2u$$
$$y = b\sin u - \tfrac{1}{2}b\sin 2u \qquad 0 \leq b \leq a$$

is placed in the stream of fluid and held at rest. The presence of the cylinder will disturb the motion represented by W_0, described above. Suppose

$$W_1 = \phi_1 + i\psi_1$$

represents the disturbing effect of the cylinder, so that the motion in the presence of the cylinder is given by

$$W = W_0 + W_1.$$

Then ψ_1 must be a solution of Laplace's equation evanescent on the circle at infinity, without singularities between the curve c and the circle at infinity, and, finally, on the curve c $\psi_0 + \psi_1$ must be constant.

Now, on the curve c,

$$z = x + iy$$
$$= a\cos u + ib\sin u + \tfrac{1}{2}b\,e^{-2iu}.$$

Then taking the transformation

$$z = a\cos w + ib\sin w + \tfrac{1}{2}b\,e^{-2iw},$$

where $w = u + iv$, we ensure that on the curve c, $v = 0$. Further,

$$z = \tfrac{1}{2}(a+b)\,e^{iw} + \tfrac{1}{2}(a-b)\,e^{-iw} + \tfrac{1}{2}b\,e^{-2iw},$$

and consequently, on the circle at infinity, $v = -\infty$.

Now, in terms of u, on the curve c,

$$\psi_0 = -q_0\{b\sin u\cos\gamma - a\cos u\sin\gamma - \tfrac{1}{2}b\sin(2u+\gamma)\}.$$

If now we write

$$\psi_1 = -q_0\{b\cos\gamma\, e^{v}\sin u - a\sin\gamma\, e^{v}\cos u - \tfrac{1}{2}b\,e^{2v}\sin(2u+\gamma)\},$$

ψ_1 is certainly a solution of Laplace's equation, which is evanescent on the circle at infinity and without singularities between c and the circle at infinity, and, in addition, on the curve c

$$\psi_1 = (\psi_1)_{v=0} = q\{b\cos\gamma\sin u - a\sin\gamma\cos u - \tfrac{1}{2}b\sin(2u+\gamma)\}.$$

Thus, $\psi_0 + \psi_1$ is zero on the curve c. We therefore have ψ_1 as above, and in consequence

$$W_1 = -q_0\{b\cos\gamma\, e^{-iw} + ia\sin\gamma\, e^{-iw} - \tfrac{1}{2}b\,e^{-2iw-i\gamma}\}$$

and

$$\phi_1 = -q_0\{b\cos\gamma\, e^{v}\cos u + a\sin\gamma\, e^{v}\sin u - \tfrac{1}{2}b\,e^{2v}\cos(2u+\gamma)\}$$

Also

$$W = -q_0 z e^{-i\gamma}$$
$$= -q_0 e^{-i\gamma}\{a\cos w + ib\sin w + \tfrac{1}{2}e^{-2iw}\}.$$

Therefore

$$W = W_0 + W_1$$
$$= -q_0(a+b)\cos(w-\gamma),$$

giving

$$\phi = -q_0(a+b)\cos(u-\gamma)\cosh v,$$
$$\psi = q_0(a+b)\sin(u-\gamma)\sinh v.$$

The velocity q at any point u on the curve is given by

$$q = -q_0(a+b)\sin(u-\gamma)\,/\,|\,dz/dw\,|\,v = 0$$

in the direction u increasing, *i. e.* along the arc of the curve. Now,

$$dz/dw = i\{\tfrac{1}{2}(a+b)e^{iw} - \tfrac{1}{2}(a-b)e^{-iw} - be^{-2iw}\}.$$

Thus on the curve c

$$|\,dz/dw\,|^2 = |\,dz/dw\,|^2_{v=0} = (a\sin u + b\sin 2u)^2 + (b\cos u - b\cos 2u)^2.$$

Evidently at $u=0$, $dz/dw|$ vanishes and the velocity is infinite except in the particular case when $\gamma=0$, that is, when the direction of streaming in the undisturbed field is parallel to the tangent to the curve at the cusp.

2. *Translational Motion.*

We may also investigate the motion represented by this W-function,

$$W_1 = q_0\{b\cos\gamma e^{-iw} + ia\sin\gamma e^{-iw} - \tfrac{1}{2}be^{-2iw}\},$$

alone. It is obtained by superposing on W, the W-function W_0. Thus, it represents the motion when the cylinder is moving in a fluid at rest at infinity with a velocity q_0 in a direction opposite to the direction of the streaming in the undisturbed field discussed in the foregoing case, *i. e.* in the direction making an angle $\pi+\gamma$ with the axis of x. The stream function and velocity potential for this motion are given by

$$\psi_1 = q_0\{b\cos\gamma e^{v}\sin u - a\sin\gamma e^{v}\cos u - \tfrac{1}{2}be^{2v}\sin(2u+\gamma)\},$$
$$\phi_1 = -q_0\{b\cos\gamma e^{v}\cos u + a\sin\gamma e^{v}\sin u - \tfrac{1}{2}be^{2v}\cos(2u+\gamma)\}.$$

The velocity at any point u is q given by

$$q^2 = \{(\partial\phi_1/du)^2 + (\partial\phi_1/dv)^2\}\,/\,|\,dz/dw\,|_{v=0},$$

and again, the velocity at the cusp is in general infinite.

The kinetic energy of the fluid per unit length T is given by

$$\begin{aligned}\mathrm{T} &= -\tfrac{1}{2}\rho\int_c \phi\, d\psi \\ &= \tfrac{1}{2}\rho q^2\int_0^{2\pi}(b\cos\gamma\cos u + a\sin\gamma\sin u - \tfrac{1}{2}b\cos(2u+\gamma)) \\ &\qquad \times (b\cos\gamma\sin u + a\sin\gamma\cos u - b\cos(2u+\gamma))du \\ &= \tfrac{1}{2}\rho q^2\pi(b^2\cos^2\gamma + a^2\sin^2\gamma + \tfrac{1}{2}b^2).\end{aligned}$$

The area of the cross-section of the curve c is A, given by

$$\begin{aligned}\mathrm{A} &= \tfrac{1}{2}\int_0^{2\pi}(x\,dy/du - y\,dx/du)du \\ &= \tfrac{1}{2}b\int_0^{2\pi}\{(a\cos u + \tfrac{1}{2}b\cos 2u)(\cos u - \cos 2u) \\ &\qquad + (\sin u - \tfrac{1}{2}\sin 2u)(\alpha\sin u + \beta\sin 2u)\}du \\ &= \pi b(a - \tfrac{1}{2}b).\end{aligned}$$

Thus

$$\mathrm{T} = \tfrac{1}{2}\rho q^2\mathrm{A}\{\mu_x\cos^2\gamma + \mu_y\sin^2\gamma\},$$

with

$$\begin{aligned}\mu_x &= \tfrac{3}{2}b/(a - \tfrac{1}{2}b), \\ \mu_y &= (a^2 + \tfrac{1}{2}b^2)/b(a - \tfrac{1}{2}b).\end{aligned}$$

The constants μ_x and μ_y may be called the coefficients of translational mass in the x-direction and in the y-direction associated with the cylinder whose cross-section is the curve c. We give a table of the coefficients μ_x and μ_y for various values of the proper fraction b/a.

b/a.	μ_x.	μ_y.
0	·0000	∞
1	·1579	10·5789
2	·3333	5·6667
3	·5294	4·0980
4	·7500	3·3750
5	1·0000	3·0000
6	1·2857	2·8243
7	1·6154	2·7346
8	2·0000	2·7500
9	2·4545	2·8384
10	3·0000	3·0000

It will be remarked in this table that for the cusped hypocycloid given by $b/a = 1$ the values of μ_x and μ_y are the same.

This result involves the consequence that in every direction whatever the coefficient of hydrodynamical mass due to translational motion is the same. This result is a particular case of the general theorem that if c the curve of the cross-section repeats itself n times on a complete description, where n is greater than two, the coefficient of hydrodynamical mass due to translational motion in any direction is the same. For suppose that μ_x and μ_y are the coefficients associated with two perpendicular directions. Then the coefficient associated with a direction making an angle $2\pi/n$ with the first is given by

$$\mu_x \cos^2 2\pi/n + \mu_y \sin^2 2\pi/n.$$

But this must be identically equal to μ_x itself, owing to the symmetry of the curve. Therefore

$$\mu_x \cos^2 2\pi/n + \mu_y \sin^2 2\pi/n = \mu_x,$$

and the conclusion that μ_x and μ_y are equal follows. Now the hypocycloid with three cusps which we deal with when a and b are equal repeats itself three times, and it consequently follows that the two coefficients associated with the direction z and y and the coefficients associated with any other direction whatever are equal.

It will further be noticed that μ_y as a function of the proper fraction b/a, which it will be convenient to call λ, has a minimum near the value $\lambda = \cdot 7$. We have, in fact,

$$\mu_y = (2a^2 + b^2)/b(2a - b)$$
$$= (2 + \lambda^2)/\lambda(2 - \lambda).$$

Then $d\mu_y/d\lambda = 0,$

when $2(2-\lambda) = 2(2+\lambda^2)(1-\lambda)/(2\lambda - \lambda^2)^2,$

i.e. when $\lambda = 1$ or

$\lambda^2 + 2\lambda - 2 = 0,$

i.e. when $\lambda = \pm \sqrt{3} - 1.$

The significance value of λ is evidently $\sqrt{3} - 1 = \cdot 7321$.

3. *Rotating Cylinders.*

Suppose that this cylinder whose cross-section is the curve c is rotating with uniform angular velocity ω about its axis. The stream function ψ associated with the motion must be a solution of Laplace's equation, as before, and evanescent at infinity and without singularities between c

and the circle at infinity. Further we must have

$$\psi + \tfrac{1}{2}\omega r^2$$

constant on the curve c. Now in terms of u, on the curve c,

$$\begin{aligned} r^2 &= (a\cos u + \tfrac{1}{2}b\cos 2u)^2 + (b\sin u - \tfrac{1}{2}b\sin 2u)^2 \\ &= a^2\cos^2 u + b^2\sin^2 u + \tfrac{1}{4}b^2 + ab\cos u\cos 2u - b^2\sin u\sin 2u \\ &= \tfrac{1}{2}a^2 + \tfrac{3}{4}b^2 + \tfrac{1}{2}(ab-b^2)\cos u + \tfrac{1}{2}(ab+b^2)\cos 3u \\ &\qquad + \tfrac{1}{2}(a^2-b^2)\cos 2u. \end{aligned}$$

Thus writing

$$\begin{aligned} \psi = -\omega\{&\tfrac{1}{4}b(a-b)e^v\cos u + \tfrac{1}{4}(a^2-b^2)e^{2v}\cos 2u \\ &+ \tfrac{1}{4}b(a+b)e^{3v}\cos 3u\} \end{aligned}$$

we obtain a value for ψ which satisfies all the conditions We therefore have also

$$\begin{aligned} \phi = -\omega\{&\tfrac{1}{4}b(a-b)e^v\sin u + \tfrac{1}{4}(a^2-b^2)e^{2v}\sin 2u \\ &+ \tfrac{1}{4}b(a+b)e^{3v}\sin 3u\}. \end{aligned}$$

At any point u on the curve the velocity q is given by

$$\begin{aligned} q = -\omega\{&\tfrac{1}{4}b(a-b)\cos u + \tfrac{1}{2}(a^2-b^2)\cos 2u \\ &+ \tfrac{3}{4}b(a+b)\cos 3u\}/\mid dz/dw\mid_{v=0}. \end{aligned}$$

The velocity is evidently infinite at the cusp $u=0$, for at that point q is given by

$$q = (q)_{u=0} = -\omega(ab+\tfrac{1}{2}u^2)/\mid dz/dw\mid_{u=v=0}.$$

It will be remarked that this infinity in q at the cusp, since it arises from the zero of $\mid dz/dw\mid_{v=0}$ at that point, is of the same type as the infinity for q in the case of translational motion.

The kinetic energy of the liquid due to the rotation of the liquid T say per unit length is given by

$$\begin{aligned} \mathrm{T} &= -\tfrac{1}{2}\rho\int\phi d\psi \\ &= \tfrac{1}{32}\rho\omega^2\int_0^{2\pi}(b(a-b)\sin u + (a^2-b^2)\sin 2u + b(a+b)\sin 3u) \\ &\qquad \times (b(a-b)\sin u + 2(a^2-b^2)\sin 2u + 3b(a+b)\sin 3u)du \\ &= \tfrac{1}{32}\pi\rho\omega^2\{b^2(a-b)^2 + 2(a^2-b^2)^2 + 3b^2(a+b)^2\} \\ &= \tfrac{1}{16}\pi\rho\omega^2\{a^4 + 2ab^3 + 3b^4\}. \end{aligned}$$

We may introduce ν by the equation

$$\mathrm{T} = \tfrac{1}{2}\nu\rho\mathrm{A}k^2\omega^2$$

where k is the radius of gyration of unit length of the

cylinder about its axis and call ν the coefficient of hydrodynamical mass associated with rotation. Then

$$Ak^2\nu = \frac{\pi}{8}(a^4 + 2ab^3 + 3b^4).$$

It is convenient to record here the value of k for the particular series of cross-sections dealt with in this paper. We have, if k_x and k_y are the radii of gyration about the axis of x and y

$$\begin{aligned}
Ak_x^2 &= \int_0^{2\pi} y^2 x\,dx \\
&= b^3 \int_0^{2\pi} [\sin^2 u + \tfrac{1}{4}\sin^2 2u - \sin u \sin 2u][a\cos u \\
&\qquad + \tfrac{1}{2}b\cos 2u][\cos u - \cos 2u]\,du \\
&= b^3 \int_0^{2\pi} [\tfrac{5}{8} - \tfrac{1}{2}\cos 2u - \tfrac{1}{8}\cos 4u - \tfrac{1}{2}(\cos u - \cos 3u)] \\
&\qquad \times [\tfrac{1}{2}(a - \tfrac{1}{2}b) + \tfrac{1}{2}a\cos 2u - \tfrac{1}{4}b\cos 4u \\
&\qquad + \tfrac{1}{2}(\tfrac{1}{2}b - a)(\cos u + \cos 3u)\,du \\
&= b^3\pi[\tfrac{5}{8}(a - \tfrac{1}{2}b) - \tfrac{1}{4}a + \tfrac{1}{32}b] \\
&= b^3\pi[\tfrac{3}{8}a - \tfrac{9}{32}b] \\
&= 3b^3\frac{\pi}{32}(4a - 3b).
\end{aligned}$$

Next, in the same manner we may prove that

$$Ak^2y = \tfrac{1}{32}b\pi(8(a^3 - a^2b) + 4ab^2 - b^3).$$

Thus

$$\begin{aligned}
Ak^2 &= Ak_x^2 + Ak_y^2 \\
&= \frac{\pi b}{16}(4(a^3 - a^2b) + 8ab^2 - 5b^3).
\end{aligned}$$

We therefore have the result

$$v = 2(a^4 + 2ab^3 + 3b^4)/b(4a^3 - 4a^2b + 8ab^2 - 5b^3),$$

or in terms of the proper fraction $\lambda = b/a$,

$$v = 2(1 + 2\lambda^3 + 3\lambda^4)/\lambda(4 - 4\lambda + 8\lambda^2 - 5\lambda^3).$$

4. *Circulation about a Cylinder.*

Suppose that there is circulation k round the cylinder of cross-section c. Then the motion may be represented by the function

$$W = \phi + i\psi = +\frac{k}{2\pi}(u + iv) = +\frac{k}{2\pi}w,$$

where, as before,

$$z = a\cos w + ib\sin w + \tfrac{1}{2}be^{-2iw}.$$

For, if ϕ be the velocity potential, the circulation is given by

$$\int_c -\partial\phi/\partial s\, ds$$

and this is equal to

$$-\int_0^{2\pi} \frac{k}{2\pi} ds,$$

which is evidently equal to $-k$. The velocity q at any point on the cylinder is given by

$$q = -k/2\pi \mid dz/dw \mid_{v=0}$$

in the direction of the arc of the curve, measured with u increasing. Again we have an infinity for the velocity q at the cusp $u=0$, and again this infinity is of precisely the same type as in the problems of translational and rotational motion.

5. *Mixed Motions.*

It has been pointed out that when a cylinder rotates about its axis or when there is circulation about the cylinder, the existence of the cusp on the curve c of its cross-section involves an infinite velocity at that point. This has also been shown to be the case when there is translational motion past the cylinder, except in the particular case when the direction of the streaming at a great distance is parallel to the tangent to the curve c at the cusp.

Now, in all these cases where the velocity is infinite at the cusp, it is infinite like

$$1/ \mid dz/dw \mid_{v=u=0}.$$

Linear combinations of these three pure types of motion therefore evidently exist in which the velocity at the cusp is no longer infinite as it is, in general, in motions of the pure types when they occur separately. Thus suppose we consider a *mixed* motion in which circulation about the cylinder is superposed on streaming past. We may superpose the motion of (2) on the motion of (4), and we then get

$$W = -q_0(a+b)\cos(w-\gamma) + kw/2\pi,$$

giving

$$\phi = -q_0(a+b)\cos(u-\gamma)\cosh v + \kappa u/2\pi.$$

Then on the curve c

$$-\partial\phi/\partial u = -(q_0(a+b)\sin(u-\gamma) + \kappa/2\pi), \qquad \partial\phi/dv = 0,$$

and

$$\mid dz/dw \mid^2 = (a\sin u + b\sin 2u)^2 + b^2(\cos u - \cos 2u)^2.$$

Thus q on the curve is given by

$$q = -(q_0(a+b)\sin(u-\gamma) + k/2\pi)/|dz/dw|_{v=0},$$

and, in general, q is infinite at the cusp $u=0$.
If the ratio of k to q_0 is so chosen that

$$k = +2\pi q_0(a+b)\sin\gamma$$

the velocity at the cusp is not infinite. We have, in fact,

$$q = q_0(a+b)(\sin(u-\gamma) + \sin\gamma)/|dz/dw|_{v=0},$$

so that at the cusp

$$q^2 = (q^2)_{u=0} = [q_0(a+b)\cos\gamma/(a+2b)]^2.$$

With this combination of translational motion and circulation an interesting type of motion results in which the velocity is never infinite on the curve c and, indeed, never infinite outside the curve. And it is to be remarked that this characteristic of the motion can be retained, whatever the direction of the translational velocity, by suitably choosing the ratio of k to q_0.

It is well known * that streaming past a cylinder together with circulation about the cylinder gives rise to a resultant force on the cylinder which is equal to $\rho k q_0$ per unit length, where ρ is the density of the surrounding fluid. And this force acts in a direction $\pi/2$ from the direction of streaming at a great distance measured in the direction opposite to that of the positive circulation. This force may be called the Lift on the cylinder. It is interesting to notice the fact that classical hydrodynamics gives a resultant force on the cylinder in this mixed motion which further has the important characteristic that the velocity of the cylinder is always finite. An important part of the requirements of the aerodynamics relating to the wings of aeroplanes is therefore satisfied before the viscosity of the air is taken into account at all; for on the one hand there is a resultant force on the cylinder, although in the case of all pure motions there is none, and on the other hand the velocity being never infinite may under suitable circumstances be kept within reasonable limits and the pressure p given by

$$p_0 - p = \tfrac{1}{2}\rho(q^2 - q_0^2)$$

(where p_0 is the pressure at a great distance) will never be

* See Lamb, 'Hydrodynamics' (5th edition), pp. 76, 647; also Joukowsky, *loc. cit.* chapter vi. § 18.

negative, and we are therefore dealing with a motion which in this respect at least is physically possible in an inviscid fluid. This fact is the analytical basis of the famous Joukowsky assumption in the Circulation Theory of Lift now under discussion in Aerodynamics *.

It is also evident that translational and rotational motion can be combined so as to give an everywhere finite velocity. For superposing the rotational motion of (3) on the translational velocity of (2) we have

$$\phi = -q_0\{(b\cos\gamma\cos u + a\sin\gamma\sin u)e^v - \tfrac{1}{2}be^{2v}\cos(2u+\gamma)\} - \omega\{\tfrac{1}{4}b(a-b)e^v\sin u + \tfrac{1}{4}(a^2-b^2)e^2\ \sin 2u + \tfrac{1}{4}b(a+b)e^{3v}\sin 3u\}$$

Evidently if we choose the ratio of ω to q_0, so that

$$\omega(\tfrac{1}{2}a^2+ab) = -q_0(a+b)\sin\gamma,$$

q, the velocity, will not be infinite at the cusp. Thus with the particular combination of translational motion q_0 in any direction γ with the appropriate rotational motion with angular velocity ω given by

$$\omega = -\frac{2(a+b)}{a(a+2b)}q_0\sin\gamma,$$

the velocity q is always finite and another type of motion is therefore available in which an infinite velocity is not associated with the cusp on the cross-section of the cylinder.

It is also evidently possible to combine circulation and rotation in the same way, so as to obtain a motion in which the velocity is everywhere finite—and this in spite of the cusp on the curve of cross-section of the cylinder.

* The assumption of Joukowsky should be studied in connexion with the pioneer work of Lanchester. See F. W. Lanchester, 'Aerodynamics,' London, 1911, § 189.

Excellent material obtained from actual experiments with full sized aerofoils and with model aerofoils suitable for the testing of the Lanchester-Joukowsky theory of Litt is to be found in 'Aeroplane Design,' by Andrews and Benson, London, 1920, chapter iii. 'The Properties of Aerofoils and Aerodynamic Bodies,' by Judge, London, 1917, chapter ii., and in other text-books.

CVIII. *The Diffusion of Mercury and of Iodine Vapours through Nitrogen.* *By* J. M. Mullaly *and* H. Jacques *.

DIFFUSION of the vapours arising from liquids or solids and passing through various gases is well known to give statistical measures of the mechanical interactions of the molecules concerned. Few elementary vapours have been investigated in this respect, because it has been difficult to experiment with substances slightly volatile. Following the speculations of Stefan (*Wien. Ber.* lxv. p. 323, 1872), the vapours of water and of many carbon compounds were early investigated by Winkelmann (*Ann. d. Physik*, xxii. p. 1, 1884 and vols. following). Lately Le Blanc and Wuppermann (*Zeit. f. Phys. Chem.* xci. p. 143, 1916) have determined the rates of evaporation of similar liquids in air under more refined conditions.

The present investigation, mentioned already in a summary account (Mullaly, 'Nature,' cxiii. p. 711, 1924), is undertaken primarily as a test of an experimental method, prior to the application of this method to further problems of diffusion.

The Method.

For establishing the gradients of vapour concentration necessary for diffusion in a steady state along a uniform tube, advantage has been taken of chemical combination between two diffusing vapours, and the consequent precipitation of both as solid products.

The two vapours, of mercury and of iodine, are allowed to diffuse from the free elements situated at the opposite ends of a closed glass tube containing nitrogen. As fast as the vapours diffuse towards one another, they combine and deposit the iodides of mercury in a region of the tube where they meet.

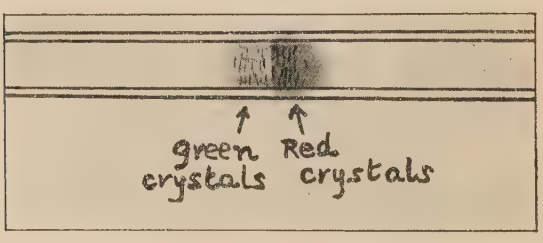
The deposit appears first as a narrow ring across the axis of the tube. On increasing in bulk, the ring spreads into a band of width comparable with the diameter of the tube, and can then be seen to contain both mercuric and mercurous iodides, the former in red crystals on the side where iodine exceeds in concentration, the latter in yellow-green crystals on that where mercury predominates. Fig. 1 is a diagram of a typical deposit. As there depicted, crystals of the two colours are separated by a very definite boundary.

* Communicated by Prof. F. A. Lindemann, F.R.S.

For a knowledge of the gradients, it is necessary to measure the distance of the deposit from the ends of the tube, that is from the points of vaporization, and, in addition, to know the concentrations (or partial pressures) of each diffusing vapour at the points of vaporization and deposition.

The concentration of mercury vapour over the meniscus has been taken from the vapour-pressure measurements of Knudsen (1909) and of Haber (1914), together with those of Egerton (Phil. Mag. xxxiii. p. 33, 1917, and later communications). There seems now to be little uncertainty as to the vapour-pressure of mercury.

Fig. 1.



Over the iodide deposit in the region where combination occurs, the concentration of mercury vapour is taken to be zero. From the determinations of the vapour-pressure of mercuric iodide by Wiedemann, Stelzner, and Niedeschulte (*Ber. Deut. phys. Ges.* iii. p. 161, 1905), it is evident that the concentration of mercury is negligibly small over portions of the deposit consisting of this salt. The concentration of mercury may be slightly greater over portions of the deposit which contain mercurous iodide, and there are few data to which reference could be made. That the concentration cannot be much greater is shown by the fact that the mercurous iodide is plentifully deposited beside the mercuric salt.

The concentration of iodine vapour over the iodine crystals has been computed as a mean from the direct measurements of Baxter, Hickey, and Holmes (Journ. Amer. Chem. Soc. 1907), and those of Naumann (Diss., Berlin, 1907), determined in the laboratory of Nernst.

The maximum concentration of iodine at the deposit has been ignored.

Mercury is effectively absent from the region traversed by diffusing iodine, the dissociation constant of mercuric iodide being extremely small. Similarly the region traversed

by mercury vapour is sensibly free from iodine. Each vapour thus diffuses through nearly pure nitrogen.

According to equation

$$D_{12}\frac{\partial c_1}{\partial l}=\frac{1}{A}\frac{\Delta m_1}{\Delta t}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which represents diffusion through one another of two gases crossing a given cross-section A of a long uniform tube, it is requisite for the determination of the coefficient D_{12} to know both the mass Δm_1 of either gas which traverses the area in a short period Δt, and the gradient of concentration of the same gas $\frac{\partial c_1}{\partial l}$ across this area. The coefficient D_{12} and the gradient $\frac{\partial c_1}{\partial l}$ are constant along the axis, so long as the concentration of the gas denoted by suffix I (the vapour) is everywhere small compared with that of the other (nitrogen).

Further, as shown by Stefan (*loc. cit.*), when the diffusion medium is kept stationary during the steady flow of the vapour, the mass of the latter traversing the area A in period Δt is larger than Δm_1 in the ratio $1+\frac{c_1}{c_2}$: 1, where c_1 and c_2 are the concentrations of vapour and gas in the plane of the area. Thus

$$D_{12}\frac{c_2+c_1}{c_2}\frac{\partial c_1}{\partial l}=\frac{1}{A}\frac{M_1}{t}, \quad . \quad . \quad . \quad . \quad (2)$$

where M_1 denotes the mass of vapour crossing the area after time t from commencement of the steady flow and under the local gradient $\frac{\partial c_1}{\partial l}$.

It is an advantage of the conditions of the present investigation that c_1 in the case of either vapour is so small compared with c_2 in any region of the tube that the term $\frac{c_2+c_1}{c_2}$ may be considered as unity and the gradient $\frac{\partial c_1}{\partial l}$ as constant.

The well-known complications in the general integration of equation (2) are avoided; and in this case

$$D_{12}\frac{C_1}{l}=\frac{1}{A}\frac{M_1}{t}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where C_1 is the saturation concentration of the given vapour,

and l the distance traversed by it from its source to the place of deposit. The errors in the values of D_{12} caused by this neglect of the quotient $\frac{c_1}{c_2}$ range from 1 in 100,000 to 0·1 per cent. in the case of mercury, and from 0·1 per cent. to 1 per cent. in the case of iodine.

Ratios of the coefficients of diffusion through nitrogen of the two vapours are measured with extreme ease and accuracy by the present method, for the vapours diffuse simultaneously in the same tube at equal temperature and pressure. Ratios of this type must have importance, since they compare certain properties of the molecular species without reference to absolute molecular concentrations. Consider the two specific equations representing the diffusion in a single tube :

$$D_{HgN}\frac{C_{Hg}}{l}=\frac{1}{A}\frac{M_{Hg}}{t} \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

and

$$D_{IN}\frac{C_I}{l'}=\frac{1}{A'}\frac{M_I}{t'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3b)$$

When the tube is uniform, $A=A'$.

Since the period of steady flow starts and ends simultaneously at the two ends of the tube, $t=t'$.

Hence

$$D_{HgN}\frac{C_{Hg}}{l}=D_{IN}\frac{C_I}{l'}\frac{M_{Hg}}{M_I} \quad . \quad . \quad . \quad . \quad (4)$$

It is found (*vide infra*) that the mercury and iodine are deposited in a nearly constant ratio by weight at a given temperature. That is, the salts composing the deposit are formed in a ratio apparently independent of the pressure of inert gas and of the dimensions of the tube. The ratio $\frac{M_{Hg}}{M_I}$ in equation (4) has thus been assumed equal to, that is to say, extrapolated from, the values found in absolute determinations.

Equation (4) thus gives the required ratio $\frac{D_{HgN}}{D_{IN}}$ from measurements of length and the vapour-pressures * alone. Such relative determinations can be made under conditions of high nitrogen pressure or of low temperature which would render any absolute determinations difficult and slow.

* Conversely, the method might be used for determining vapour-pressures from a knowledge of coefficients of diffusion together with two measurements of length.

The ratio $\frac{D_{HgN}}{D_{IN}}$ as measured compares the diffusion of the two vapours under strictly similar conditions of gradient, even though the vapour-pressure of iodine greatly exceeds that of mercury. Under no circumstances could M_{Hg} differ largely from M_I, nor D_{Hg} from D_{IN} in a single tube, so that from (3) $\frac{C_{Hg}}{l}$ and $\frac{C_I}{l'}$ are of comparable magnitude. If under some hypothetical condition mercuric iodide were alone deposited, then $\frac{M_I}{M_{Hg}}=2$ in atomic units; if the mercurous salt were alone to appear, M_I and M_{Hg} would be atomic equivalents.

Owing to the large difference between the vapour-pressures of the two elements, the deposit occurs on the side of the tube close to the mercury and remote from the iodine. Measurement of the length traversed by the mercury is thus the more difficult. For more convenient measurement of this length, as is desirable in the case of the absolute measurements of diffusion, two alternative schemes are suggested, namely :—

(1) A source of iodine vapour other than crystals of the free element, and such as to supply the vapour at a constant and suitably low pressure. The tri-iodide of cæsium CsI_3 would appear suitable from the investigation of this substance by Abegg and Hamburger (*Zeit. Anorg. Chem.* l. p. 403, 1906). It has not yet been used owing to the adoption of the second method.

(2) Alternatively to constrict the tube along the region traversed by iodine vapour, and thus by diminishing A′ on the right-hand side of equation :

$$D_{HgN}\frac{\partial c_{Hg}}{\partial l}\frac{A}{M_H}=D_{IN}\frac{\partial c_I}{\partial l}\frac{A'}{M_I}$$

to cause the variable $\frac{\partial c_{Hg}}{\partial l}$ to diminish on the left through an increase in the length traversed by mercury.

This device has been used for all the absolute measurements with mercury. Tubes so constricted are unsuitable for obtaining simultaneously values for iodine, because over the region of constriction the gradient $\frac{\partial c_I}{\partial l}$ must vary. It

would be difficult to trace the gradient from place to place directly.

Tubes of one metre total length are convenient. The constriction may take the form of a capillary, and should not offer so great a resistance as to make the deposit thin and indistinct, for increasing the distance traversed by the vapours has the effect of somewhat spreading out the deposit *.

The design of the tube is important in another respect. The tube-walls must offer some resistance to the flow of the vapours, and this effect is superimposed upon the resistance of diffusion. The effect might be corrected for according to the laws of transpiration, but since it is small, even in the case of the narrowest tubes used, no correction has been applied.

For measurement of absolute values, a tube of 3-mm. bore is suitable, since this gives the greatest cross-section compatible with stability of the mercury meniscus at one end, or of an adherent sublimate of iodine at the other. A wide tube has the additional advantage of affording more deposit in a given time.

In relative determinations for which small deposits suffice, narrower tubes are preferable, since these give the better definition required for measurements of length. Capillaries of 1 mm. have been found best in this case.

Care must be taken to avoid contamination of either element by traces of the iodide deposit. In cases where the deposit forms in close proximity to the mercury, and especially in tubes of wide bore, there is a tendency for precipitation on the meniscus. Contamination in such cases is avoided by imparting a quivering motion to the meniscus, the tube being gently rocked. Rocking was performed in the vertical plane containing the axis of the tube, while care was taken that the end containing the mercury was always slightly the lower in level. In order that the rocking may be the more effective, there was a small gas space behind the mercury, for the tube was bent up in the form of a crook.

As regards the pressure of the gas, certain limitations must be observed. Since the rate of diffusion varies inversely as the pressure, it is necessary, for securing sufficient deposit in a reasonable time, to keep the pressure low. Especially in constricted tubes should the pressure be low, for in these the mercury has a greater distance to

* In the limit resolving the deposit into *two* isolated bands. Details of this will be published later.

diffuse. But too low a pressure leads to spreading of the deposit by diffusion of its vapour, especially when the tube is wide. Pressures of 1 mm. to 10 mm. were used for the absolute values, and pressures up to 17 cm. for the relative values. For purposes in view it matters little what range of pressure is considered so long as the pressure is large in comparison with the partial pressures of the vapour, and yet low enough for the simple gas laws to hold.

A source of small error difficult to avoid is the mixing of the vapours and gas before the measurement of pressure P_N. The effect due to mercury is negligible. The iodine may increase the pressure by 0·1 mm., that is by about half the saturation pressure P_I, since its gradient extends along the tube. Further, after the final sealing, vaporization of the iodine must increase the partial pressure of nitrogen in the mercury end of the tube. Both kinds of effect are less for the constricted tubes, and in any case tend to cancel on the side of the tube containing mercury. They may together amount to 1 per cent. of the lowest pressures recorded, but were in all cases ignored.

In no case was more than 0·2 mg. of nitrogen contained in a tube. For economy therefore, also by reason of the stationary condition of the gas, the present method has advantages over those of Winkelmann and of Le Blanc and Wuppermann, each of which methods requires a continued circulation of many litres of gas, at constant pressure, throughout the period of experiment.

Owing both to the compactness of the tube and to the slowness of the process, there is no possibility of the cooling by vaporization pointed out by Le Blanc and Wuppermann.

Experimental.

(A) *Absolute Measurements.*

Means of filling Diffusion Tube.

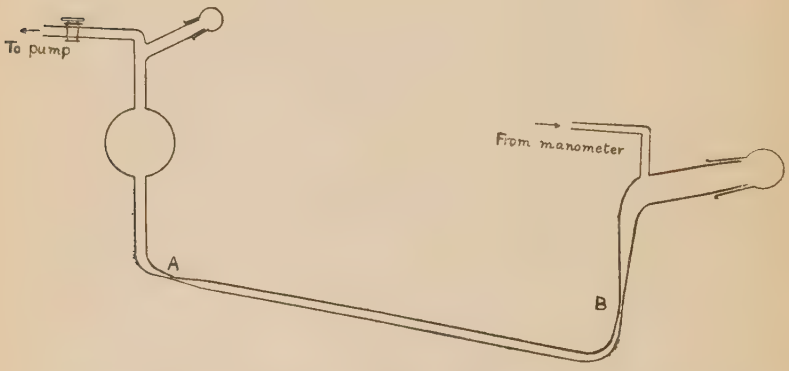
Fig. 2 shows the apparatus used. The diffusion tube, well cleaned, is sealed on at A and B and drawn down for convenient closing at these points. Iodine, of "AR" purity, is placed in the globe on the left side, while mercury—purified by electrolysis—is placed in a small iron boat in the sloping tube on the right-hand side. The iodine can be sublimed into the tube from the globe, and the mercury tipped in from the boat, an electromagnet being convenient for inverting the latter. No contamination is

thus incurred by grease or other surface film which would impede the vaporization.

Before introducing the mercury, the nitrogen is passed in and its pressure measured. The nitrogen was prepared from a commercial specimen of 99·7 per cent. purity containing very little argon. It was freed from oxygen by means of red-hot copper, and dried thoroughly. It is needless to enter into details of the purification. Traces of hydrogen were detected (derived from the heated copper), but the amount was negligible.

Exhaustion was effected by means of an oil-pump in such a sense as to cause the gas always to flow from the right-hand side to the left. This unidirectional flow is very

Fig. 2.



desirable in order to prevent iodine vapour from diffusing towards the mercury and contaminating the tube. The tube was heated to expel occluded gas and inevitable traces of mercuric iodide.

Iodine having been carefully sublimed into the tube, the pressure was measured at room temperature : high pressures on a manobarometer, and low pressures with a McLeod gauge. A correction (about 1 per cent. usually) was applied for the change in pressure due to transference to the higher temperature of the thermostat as described below.

Finally the mercury was introduced. This operation could not alter the pressure, owing to the large volume of the iodine globe.

The moment of the entrance of mercury may be taken as the starting time, since this almost coincides with the first appearance of deposit. The appearance of deposit does not mark the attainment of the steady state of flow, but this

state should not succeed it by more than an hour. Such a preliminary period is negligible in an experiment of ten days' duration. It will be remembered that in the experiments of Le Blanc and Wuppermann about one-tenth of the total time was allowed for at the start.

After sealing up, the tube was placed in a thermostat.

Temperature of Experiment.

Owing to the high temperature coefficients, both of vaporization and of diffusion, constancy of temperature is essential ; yet the deposits are well defined when formed at room temperature. Convection in the tubes, then, is slight.

The temperature was throughout maintained at 19°·4 C. in a thermostat 4 feet long containing water circulated by four propellers. Except for one or two accidents the variation was about $\pm 1/50°$ C.

The Measurements of Length.

It is required to determine the length traversed by each vapour from its source to that part (or plane) of the deposit at which the concentration gradient first begins perceptibly to vary. As will be shown in a subsequent communication, the gradients of concentration do not change greatly at the outer fringe of the deposit, for chemical combination is restricted to a comparatively thin region or lamina in the centre portion of the deposit. Some of the visible spreading is due to diffusion of the saline vapours while in a state of supersaturation. These vapours and their dissociation products can in no way influence the normal gradients, since the dissociation constants are unchanged.

It is therefore necessary to measure the lengths up to the centre portion of the deposit ; and since it is found that the two iodides fall alongside one another about a well-defined boundary, it is convenient to adopt this boundary as a mark for the measurements of length.

It is found that there is a distinct ridge of the red crystals alongside and close to the boundary. The deposit is thickest in the plane of this ridge at the temperature investigated. Since, however, we do not necessarily seek the planes across the deposit which contain the centres of gravity of the elements deposited, the presence of this ridge has been ignored in taking the measurements of length. Discussion of the detailed features of the deposit must be deferred to a future occasion.

At the ends of the tube imaginary planes must be found, from which diffusion may be assumed to commence. The mercury meniscus is a segment of a sphere. The plane cutting this segment parallel to its base and through a point bisecting its height will therefore divide the vaporizing surface into equal areas. Since these areas are nearly equidistant from the deposit, it is safe to consider this place as the effective source of vapour. After locating the base of the meniscus, a correction was thus applied for half its height. Contraction of the mercury column on removal from the thermostat was allowed for; to obviate this source of error and to diminish the risk of derangement caused by handling, an endeavour will later be made to read the lengths while the tube remains in the thermostat.

Measurements were made with the tube in four positions about its axis, the asymmetry of a meniscus in horizontal tubes being taken into account.

The short distance traversed by mercury vapour can thus be read with an accuracy of about 0·05 mm. or $\pm 0{\cdot}5$ per cent.

Definition of the iodine is secured by careful filling of the tube. Observation must be made of the slight retreat along the tube during the period of consumption. On a length of 1 metre an accuracy of $\pm 0{\cdot}2$ per cent. is certain.

After measurement the tube is opened by cutting it beside the deposit; simultaneously the period of diffusion is considered at an end.

Analysis of the Deposit.

The iodine has been determined directly, the mercury by difference.

Weighings have been conducted with great accuracy through the kindness of Mr. A. C. Egerton, whose balance has been used. The authors take this opportunity of cordially thanking him for his interest in the work.

The weighed deposit is dissolved in 10 c.c. of hydrochloric acid of 5 N strength containing 2 c.c. of 0·1 N nitric acid, Kjeldahl's apparatus being used to prevent escape of iodine. Solution is slow even when conducted in a steam bath. As the mercuric iodide dissolves the more rapidly, it can be seen how sharp is the boundary towards the other salt. When solution is complete, 2 or 3 c.c. of 0·1 N sodium sulphite are added to reduce iodate, and the mixture left to stand. The mixture then contains no mercurous compounds, and the iodine as I' ions.

The method of Fresenius ('Quant. Chemical Analysis,' vol. i. 7th ed. p. 366) was used to estimate this iodine, chloroform being used for its isolation. A deposit of

0·04 gram gives but one titration of 15 c.c. with $\frac{N}{100}$ sodium thiosulphate, but there is little danger of an overshot, since several of the chloroform extractions are needed for withdrawal of the iodine.

Cross-section of the Tube.

Short lengths from the region traversed by mercury were measured by optical examination of the cut ends, while long lengths from the iodine side were filled with mercury at the temperature of diffusion and weighed.

Commercial tubing was used, which was found sometimes to vary as much as 5 per cent. along its length. Mean values as determined cannot, however, be greatly in error.

Numerical Values.

It would be tedious to tabulate all the measurements made, since one experiment of each type will illustrate the magnitudes concerned.

Thus in an experiment upon iodine :—

Temperature of thermostat	19·40° C.
Pressure at room temperature	9·616 mm. of Hg.
„ (P_N) reduced to 19°·4	9·78 „
Length from iodine to deposit when first formed...	892·5 mm.
Retreat of iodine	2·0 „
Corrected length (l')	891·5 „
Time-interval (t) 12 days, 1 hr., 17 mins.	
Mass of iodine deposited (M_I)	0·01163 gram.
Mean cross-section of tube at 19·4° C. (A')	6·472 mm.^{2}

Therefore $D_{IN}=5{\cdot}80$ cm.^{2} sec.$^{-1}$

In one for mercury at the same temperature :—

Pressure at room temperature	5·608 mm. of Hg.
„ (P_N) reduced to 19°·4	5·65 „
Length from base of meniscus to deposit being a mean of 4 readings	20·85 mm.
Meniscus correction	0·50 „
Corrected length (l)	20·35 „
Time-interval (t) 20 days, 22 hrs., 12 mins.	
Mass of whole deposit	0·02474 gram.
„ iodine	0·01129 „
„ mercury by difference (M_{Hg})	0·01344 „
Cross section of tube over region traversed by mercury (A)	6·630 mm.^{2}

Therefore $D_{HgN}=17{\cdot}3$ cm.^{2} sec.$^{-1}$

Constriction of tube required in this experiment = 45 cm. length of 1 mm. capillary.

Iodine-Nitrogen at 19°·4 *.

Pressure of nitrogen. mm.	D_{IN} cm.^{2} sec.$^{-1}$.	$\frac{1}{P_N+\frac{1}{2}P_I}$.	$D_{IN}(P_N+\frac{1}{2}P_I)$.	Remarks.
13·7	3·99	0·0725	55·03	Preliminary experiment value low.
6·61	8·46	0·1492	56·71	Pressure doubtful.
9·52	6·05	0·1040	58·17	
7·5	7·63	0·1318	57·89	Air-leak into manometer roughly corrected for.
9·85	5·84	0·1006	58·05	
9·83	5·70	0·1008	56·55	
9·78	5·80	0·1013	57·25	Reliable.
9·27	6·33	0·1068	59·27	Cross-section uncertain; tube broken.
9·71	5·81	0·1020	56·96	Reliable.
		Weighted mean.....	57·0	

* Assumed $C_I=2{\cdot}623\times10^{-6}$ gram per c.c., corresponding to $P_I=1{\cdot}884\times10^{-1}$ mm.

Mercury–Nitrogen at 19°·4 †.

Pressure of nitrogen. mm.	D_{HgN} cm.^{2} sec.$^{-1}$.	$\frac{1}{P_N+\frac{1}{2}Hg}$.	$D_{HgN}(P_N+\frac{1}{2}P_{Hg})$.	Remarks.
5·65	17·3	0·1770	97·04	
2·55	>34·0	0·3921	>86·72	D value low tube not rocked.
2·45	39·6	0·4080	97·06	Deposit not well defined.
3·52	27·2	0·2840	95·77	Reliable.
1·97	49·5	0·5075	97·53	
3·40	27·3	0·2941	92·84	Air-leak.
		Weighted mean.....	97·0	

† Assumed $C_{Hg}=1{\cdot}32\times10^{-6}$ gram per c.c., corresponding to $P_{Hg}=1{\cdot}20\times10^{-3}$ mm.

Hence the ratio $\frac{D_{HgN}}{D_{IN}}=\frac{97}{57}=1{\cdot}70$

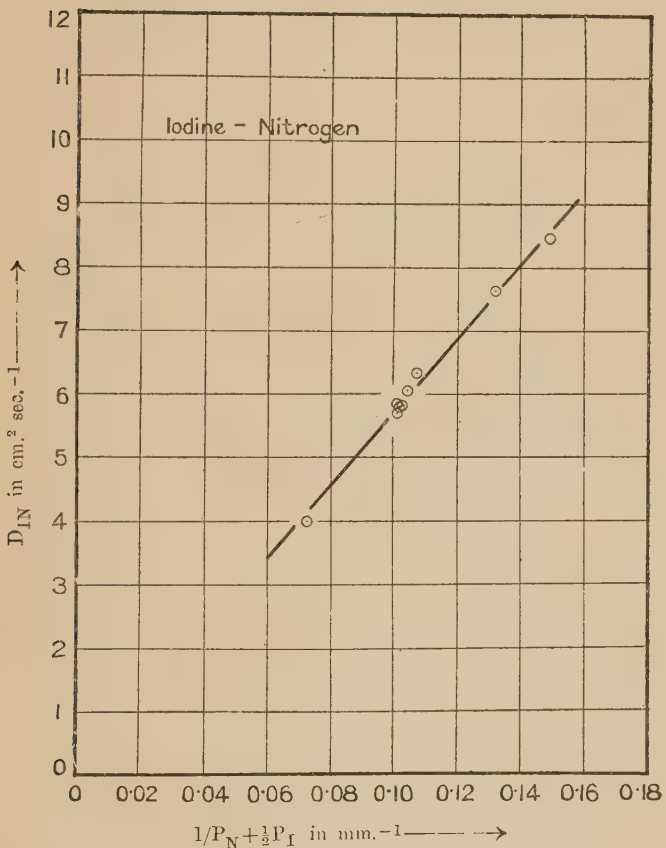
It is clear that the figures in the fourth column are in each case nearly constant.

In figs. 3 and 4 the diffusion coefficients are plotted against the reciprocals of the total pressures. P_{Hg} and P_I denote the saturation pressures of the vapours, so that $\frac{1}{2}P_{Hg}$ and $\frac{1}{2}P_I$ should represent the mean partial pressures along the regions of diffusion.

The coefficients for mercury are practically as concordant as those for iodine, but would be subject to a greater

constant error if the adopted boundary were unsuitable for the measurement of length.

Fig. 3.



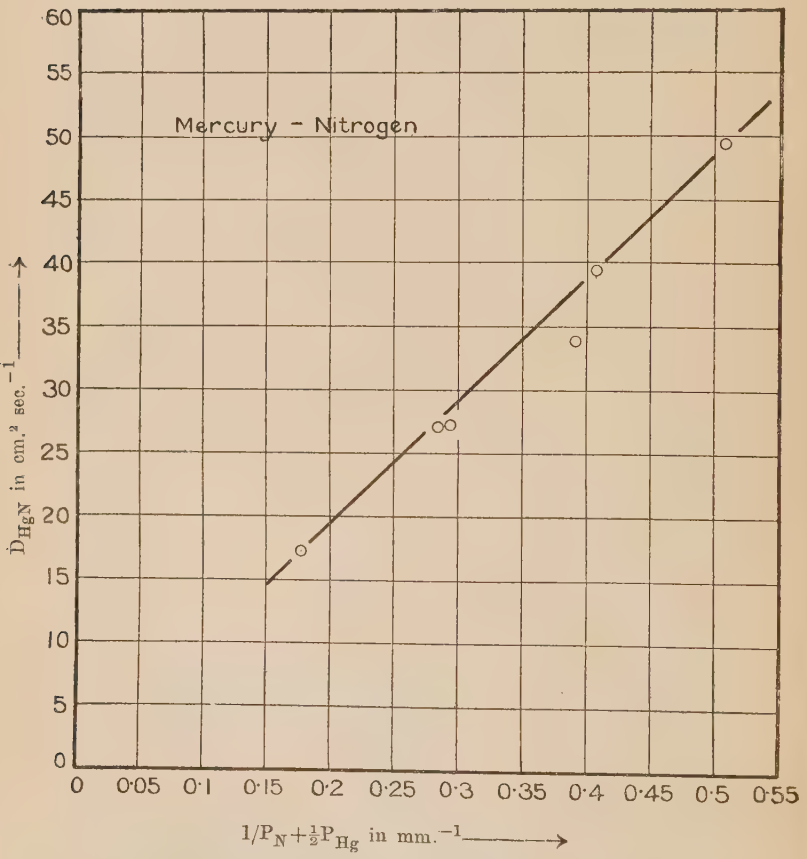
(B) *Relative Measurements.*

The relative determinations are much simpler, since they need not involve estimates of time or those of tube section, or even those of mass.

From the analysis of the deposits it has been found that the two elements are precipitated in a nearly constant ratio by weight at the given temperature. That this is so can be easily imagined, for in the hypothetical case where the amount of nitrogen is infinitely small, the rates of deposition

of the iodides would be determined solely by their dissociation pressures. (The co-precipitation of two electrolytes which possess an ion in common is closely analogous, but comparison must for the present be postponed.) The presence of the inert gas nitrogen could modify this

Fig. 4.



condition only by hindering the approach of the iodide vapours to the walls of the tube, the ratio of masses deposited being thus dependent upon the diffusivities of the iodides and of their dissociation products as well as upon their equilibrium pressures. When the diffusion effect is small, as in narrow tubes, the ratio of masses deposited must

at a given temperature be nearly independent of the total pressure. The following table shows the values found :—

Ratio of masses deposited, Hg/I.	Pressure of nitrogen. mm.
1·108	7·5
1·114	9·85
1·189	5·65
1·187	9·78
1·144	9·27
1·187	9·71
1·205	2·55
1·203	2·45
1·161	3·52
1·129	1·97
ca. 1·100	3·40
Average... 1·16	

The ratio of masses deposited is thus nearly constant under the conditions of experiment *.

Since this ratio is constant (at the temperature considered), it is requisite from equation (4) that the ratio of lengths $\frac{l'}{l}$ be likewise constant under the given conditions. The constancy of the ratio $\frac{l'}{l}$ is very rigorously shown by experience (see table below); indeed, the accuracy attainable in the measurement of length exceeds that of the chemical analysis, and affords a very real check on the uniformity of the process. The ratio of masses is uninfluenced by a constriction in either end of the tube, because this is in effect merely a lengthening of the tube, and not an alteration of the ratio $\frac{l'}{l}$ (analogous to a resistance in an arm of Wheatstone's electrical bridge).

For the relative determinations of diffusion the ratio of masses deposited has been assumed the same as in absolute determinations, while the lengths have been measured. To correct for the inevitable tapering of the tube, the measured ratio of lengths $\frac{l'}{l}$ must be divided by the ratio of the mean sections $\frac{A'}{A}$ along the corresponding regions of diffusion.

* The irregularities have subsequently been found to be due to a slow photo-chemical action of mercurous iodide. These irregularities can obviously not effect the accuracy of the absolute measurements of diffusion.

The following is a typical experiment :—

Pressure at 19·4	179·0 mm. of Hg.
Length from base of meniscus to deposit (4 readings).	6·09 mm.
Meniscus correction	0·13 „
Correction for temperature of reading	0·01 „
Mercury length corrected (l)	5·95 „
Iodine length (l')	761·5 „
Therefore ratio of lengths observed $\left(\frac{l'}{l}\right)$	128·1
Mean tube diameter	1·18 mm.
Ratio of mean cross-sections along the two regions of diffusion $\left(\frac{A}{A'}\right)$	1·015
Therefore ratio of lengths for a uniform tube $\left(\frac{l'}{l}\times\frac{A}{A'}\right)$	$=128·1\times1·015$ $=130·0$
Assumed ratio of masses deposited $\frac{M_{Hg}}{M_I}$	= 1·16
Therefore $\frac{D_{HgN}}{D_{IN}}$ at 19°·4	= 1·77

The table gives the ratios determined at 19°·4.

Tube.	Pressure total. mm.	Ratio of lengths for a uniform tube.	$\frac{D_{HgN}}{D_{IN}}$.	Remarks.
A	102	128·4	1·79	Preliminary experiment.
B	179·0	130·0	1·77	Reliable.
B again	„	128·8	1·78	
C	72·0	128·6	1·79	Pressure uncertain; iodine badly placed.
C again	„	127·5	1·80	
D	67·5	128·7	1·79	Ill-defined deposit.
D again	„	133·7	1·72	
E	79·0	128·9	1·78	Narrow tube difficult to fill; values reliable.
E again	„	130·0	1·77	
		Average	1·78	

Such experiments were repeated in the case of most tubes. The tube was reset by shaking the mercury a little further along the axis so as to produce a new deposit on the clear wall. The second deposit was usually better defined than the first, owing to microscopic crystal nuclei previously spread about, and because of the quickness of re-attainment of a steady state.

It should be observed that the application of the method to relative measurements of diffusion rests upon facts additional to those which fit the method for absolute measurements. Absolute measurements could be made whether

or not the deposit is of regular constitution, provided only it occurs in a very limited region of the tube, for equation (1) is quite determinate, as is well known, and for integration requires solely a knowledge of the distribution of concentration. The relative measurements are rendered simple, not only by the simultaneous presence of the two vapours, but by the regularity of the deposits which permits extrapolation of the ratio $\frac{M_{Hg}}{M_I}$. The corresponding ratio in the case of similar diffusion of ammonia and hydrogen chloride would be fixed stoichiometrically, since only one salt, ammonium chloride, is then possible.

The average ratio 1·78 of the coefficients of diffusion differs but slightly from the value 1·70 obtained from the absolute determinations at low pressures. The difference is probably real, since the coefficients of diffusion may vary with the proportions in which vapour and gas are mixed. But no great stress is laid upon this difference, since it is comparable with the errors of experiment. The difference is due partly to the neglect of the term $\frac{c_1}{c_2}$ in Stefan's equation (2) (meaning that 1·70 is too small a ratio), and partly to resistance offered by the narrow tubes to the flow of iodine vapour (1·78 being thus too large).

The magnitude of the mean ratio 1·74 shows that iodine diffuses more slowly than does mercury.

Interpolation from the direct observations gives for a temperature of 19°·4 C.:

$$D_{HgN}=32{\cdot}3 \text{ when } P_N+\tfrac{1}{2}P_{Hg}=3{\cdot}00 \text{ mm.}$$

and
$$\frac{P_N}{\frac{1}{2}P_{Hg}}=5{\cdot}0\times 10^3,$$

and
$$D_{IN}=5{\cdot}70 \text{ when } P_N+\tfrac{1}{2}P_I=10{\cdot}00 \text{ mm.}$$

and
$$\frac{P_N}{\frac{1}{2}P_I}=1{\cdot}06\times 10^3.$$

Discussion of these results must be postponed to a future communication.

The authors desire to express their best thanks to Professor Lindemann for his valuable advice, to Mr. A. C. Egerton, and to General H. B. Hartley of Balliol College.

also to Mr. I. O. Griffith. They acknowledge their indebtedness to the Chemical Society for a grant which has partly defrayed the cost of the investigation.

14 Bardwell Road,
Oxford.
September 1924.

[*Note added November 8th.*—A fact which further simplifies the method is that both ends of the diffusion tube may be left open to a pure atmosphere of the inert gas. No stream of the gas traverses the tube once the steady state is established, for gradients of the vapours are set up from the elements towards the open ends, and the pressure of inert gas is the same at these ends. In some experiments upon diffusion through air it has been found easy to shake the elements out of an open tube and rearrange at will.—J. M. M.]

CIX. *Pole Lines occurring in the Interrupted Arc Spectra of Silver, Gold, and Copper.* *By* H. Lowery, *M.Sc. (Lond.), A.Inst.P., F.R.A.S., Assistant Lecturer in Physics, Manchester University* *.

[Plate XXVII.]

DURING the course of an investigation on the Stark effect in the arc, the spectra of "arc flashes" between silver, gold, and copper poles in air, hydrogen, and oxygen were photographed. Of the many interesting points exhibited by the photographs, it is proposed in this paper to refer to certain lines which seem to be associated with the lower pole of the arc under the particular conditions of the experiments.

Experimental Details.

The method of making an arc flash was that used by Hemsalech and the Comte de Gramont †. The lower pole was kept fixed throughout the experiments whilst the upper pole was arranged so that by pulling a cord it could be drawn into contact with the lower pole. When the poles came into contact, the circuit was made through a key and the cord released. An arc was thus formed between the poles, but the upper pole was caused to move away quickly

* Communicated by Prof. W. L. Bragg, F.R.S.
† Phil. Mag. vol. xliii. (Feb. and May 1922).

from the lower pole to such a distance that the arc ceased to pass, so that only an arc flash was produced.

It will be convenient to speak of the arc observed in this manner as the *interrupted* arc to distinguish it from the *continuously-burning* arc.

Experiments were made under various electrical conditions and the voltage and current at contact of the poles were recorded. The voltages were varied from 100 to 400 volts and the currents when the circuit was made ranged from 0·3 to 25 amperes. Of course the intensity of the arc flashes changed considerably with these wide differences in voltage and current, thus necessitating more flashes for a photographic exposure in some of the experiments than in others. The lower pole was usually negative in the experiments, though for special tests it was made positive.

The Spectrograph.

For the purpose of this research a spectrograph was mounted in which a small Rowland grating (14,438 lines to the inch; radius of curvature 72 in.; ruled space 2 in. long) was used with a 3 in. refracting telescope as collimator. The eyepiece of the telescope was replaced by a Hilger slit which was adjusted to be at the focus of the objective so that the rays leaving the objective after passing through the collimator were parallel. The grating and camera were mounted on the same support, which turned about a point in the axis of the collimator vertically under the grating.

It will be observed that in this mounting, since parallel light is allowed to fall on the concave grating, stigmatic images of the light source are produced.

The dispersion given by the spectrograph in the first order was about 19 Å.U. per mm.

Experimental Results.

Before an experiment was begun, care was taken to focus the lower fixed pole of the arc just below the middle of the collimator slit and to arrange that each arc flash should fall along the length of the slit. The object in conducting the experiments in this manner was to obtain photographs of the spectra due to the earliest stages in the formation of a flash. Since the particular mounting of the grating employed gave stigmatic images, the effects introduced into the spectra during the initial stages of an arc flash were readily distinguished.

TABLE I. Pole Lines (Silver).

Wave-lengths in I.A.	Class.	Intensity.	Previous Observer.
3560·5 (*a*)	I	2	.....
3576·2	II	1	.....
3580·62	I	1	Eder and Valenta * : Spark.
3630·09 (*b*)	I	1	Frings † : Spark.
3630·6 (*c*)	II	1	.....
3649·82	I	2	Eder and Valenta : Spark.
3683·25	I	3	,, ,, ,,
3728·2	I	2	.....
3766·35	I	1	Exner and Haschek ‡ : Arc.
3829·3	I	1	.....
3840·80	I	3	Frings : Arc.
3877·25	I	1	Exner and Haschek : Spark.
3907·48	I	4	Kayser and Runge § : Arc.
3914·32	I	4	,, ,, ,,
3920·10	I	2	Wagner ‖ : Spark.
3945·6	II	1	.....
3985·03	I	2	Eder and Valenta : Spark.
4004·75	I	1	Exner and Haschek : Spark.
4012·3 (*d*)	II	1	.....
4063·6	I	1	.....
4068·01	I	3	Frings : Spark.
4081·7 (*e*)	I	0	Takamine ¶.
4085·90	I	1	Frings : Spark.
4141·6	II	1	.....
4182·1	II	1	.....
4206·8 (*f*)	I	0	Takamine.
4226·55 (*g*)	I	1	,,
4281·2	II	1	.....
4298·1	I	1	.....
4381·4	II	1	.....
4395·94	I	2	Frings : Spark.
4455·4	I	1	.....
4548·9	I	1	.....
4550·4	I	1	.....
4610·6	I	1	.....
4614·5	II	1	.....
4615·82	I	2	Eder and Valenta : Spark.
4620·39	I	0	,, ,, ,,
4650·3	I	1	.....
4657·2	I	1	.....
4677·86	I	2	Kayser and Runge : Arc.
4680·4	I	1	.....
4721·1	I	1	.....
4785·5	II	1	.....
4811·3	I	3	.....
4843·3	I	1	.....
4870·2	I	3	.....
4934·3	II	1	.....

* 'Atlas Typischer Spektren' (Wien, 1911).
† *Zeit. für wiss. Phot.* xv. p. 165 (1915).
‡ Tabellen der Funkenlinien (1902); Tabellen der Bogenlinien (1904).
§ Handbuch der Spectroscopie, Band V. (Leipzig, 1910).
‖ Dissertation (Bonn, 1911).
¶ Astrophys. Journ. vol. l. (1919).

Notes on Table I. (Silver).

(*a*) λ 3560·5 and (*d*) λ 4012·3.—At the beginning of the arc flash both lines are displaced to the red from their positions during the later stages, (*a*) by about 1 Å.U. and (*d*) by about 0·5 Å.U.

(*b*) λ 3630·09 and (*c*) λ 3630·6.—The latter line (not previously recorded) is displaced to the red by about 0·5 Å.U. at the making of the arc. The displacement is readily detected owing to the nearness of λ 3630·09.

(*e*) λ 4081·7, (*f*) λ 4206·8. and (*g*) λ 4226·55.—The wave-lengths of these three lines are as recorded by Takamine who, in his research on the Stark effect for silver *, records that the lines (*e*) and (*g*) only occur in a strong electric field. In the present work, all three lines are confined to the initial stages of the arc flash. In the experiments with heavy currents, the line λ 4206·8 is usually masked by a wing which accompanies the arc line λ 4210 on the violet side at the beginning of a flash.

Whether the interrupted arcs between silver, gold, and copper poles were made in air, hydrogen, or oxygen, the corresponding photographs are characterized by a number of lines which appear only during the early stages of an arc flash. These lines seem to be closely associated with the lower fixed pole and occur whether that pole is positive or negative, though they are certainly more numerous under the latter condition. For convenience, they will be termed *pole lines*: they are presumably lines which are specially enhanced under the abnormal conditions of voltage and current employed, and are possibly due to the excitation of multiply ionized atoms.

A careful study of these pole lines reveals the fact that they may be arranged into two classes as follows :—

Class I.

Whereas the ordinary arc lines cease when the poles are about 6 mm. apart, the lines of this class commence with moderate intensity and decrease gradually in intensity till they disappear when the poles are separated by about 1 to 3 mm., though the actual distance of separation of the poles at which disappearance takes place seems to depend (between the above limits) upon the value of the initial current.

Class II.

Lines comprised in this class come to an end abruptly when the poles are about 1 mm. apart. They are of uniform intensity along their lengths, and changes in the initial currents affect only their intensities and not their lengths. Their intensities seem also to depend on the voltages employed, for the lines are much stronger at 350 volts than

* *Loc. cit.* p. 26.

at 250 or 110 volts. There are 11 lines of Class II in the interrupted silver arc spectrum, 6 in the gold and 2 in the copper in the region, λ 5220 to λ 3380, covered by the research.

TABLE II. Pole Lines (Gold).

Wave-lengths in I.A.	Class.	Intensity.	Previous Observer.
3649·10	I	4	Eder and Valenta: Spark.
3706·84	I	2	,, ,, ,,
3950·04	I	1	,, ,, ,,
3959·20	I	4	,, ,, ,,
3968·7	I	5	.....
3985·89	I	2	Eder and Valenta: Spark.
3989·85	I	1	,, ,, ,,
3991·49	I	3	,, ,, ,,
3994·1	II	2	.....
4012·72	I	4	Eder and Valenta: Spark.
4027·3	II	1	.....
4028·51	I	1	Eder and Valenta: Spark.
4061·05	I	2	Exner and Haschek: Spark.
4070·61	I	3	Eder and Valenta: Spark.
4076·45	I	5	,, ,, ,,
4089·80	I	2	,, ,, ,,
4171·26	I	2	,, ,, ,,
4171·9 (*a*)	II	2	.....
4172·74	I	2	Eder and Valenta: Spark.
4227·3	I	1	.....
4229·2	I	1	.....
4260·5 (*b*)	I	2	.....
4275·84	I	1	Eder and Valenta: Spark.
4361·2	II	2	.....
4395·55	I	1	Eder and Valenta: Spark.
4467·3	II	1	.....
4558·87	I	1	Eder and Valenta: Spark.
4597·2	II	1	.....
4599·4 (*c*)	I	1	.....
4630·40	I	2	Eder and Valenta: Spark.
4633·05	I	1	,, ,, ,,
4640·54	I	0	,, ,, ,,
4643·08	I	1	,, ,, ,,
4673·06	I	1	,, ,, ,,
4902·27	I	2	,, ,, ,,
4920·32	I	1	,, ,, ,,

Notes on Table II. (Gold).

(*a*) λ 4171·9 (not previously recorded) is readily observed between the spark lines λ 4171·26 and λ 4172·74, from which it is quite separate.

(*b*) λ 4260·5 (not previously recorded) is easily distinguished from the spark line 4259·85 (intensity 1).

(*c*) λ 4599·4 usually disappears when the poles are about 2 mm. apart and is displaced to the red by 1 Å.U. at the beginning of the arc flash.

The lines of the second class do not occur in the continuously-burning arc spectra, though a few of the stronger lines of the first class appear in the neighbourhood of each pole under these conditions, being more pronounced at the negative than at the positive pole. The same lines of each class appear in the spectra of the interrupted arcs whether the arcs are made in air, hydrogen, or oxygen; but, for given electrical conditions, they are slightly more intense when the arc flashes are made in hydrogen than when they are made in air and oxygen (when the intensities are nearly equal).

It is to be particularly noted that most, though not all, of the lines of the first class have been identified with lines observed by previous experimenters in the arc or spark spectra of the respective metals, whereas the lines of the second class do not seem to have been previously recorded.

Tables I., II., and III. contain lists of the pole lines of

TABLE III. Pole Lines (Copper).

Wave-lengths in I.A.	Class.	Intensity.	Previous Observer.
3539·1 (*a*)	II?	0	.....
3595·3	II	1	.....
3597·8 (*b*)	II	2	.....
3641·693	I	3	Hasbach *: Arc.
3654·3 (*c*)	I	6	,, ,,
3684·925	I	1	,, ,,
3697·84	I	2	Eder and Valenta: Spark.
3700·41	I	2	,, ,, ,,
3737·47	I	1	,, ,, ,,
3764·75 (*d*)	I	2	Kayser and Runge: Arc.
3777·02	I	4	Eder and Valenta: Spark.
3790·97	I	2	,, ,, ,,
3807·69	I	3	,, ,, ,,
4015·8	I	1	Hasbach: Arc.
4056·7	I	4	,, ,,
4227·93	I	3	,, Spark.
4683·17	I	2	Eder and Valenta: Spark.
4758·578	I	2	Aretz †: Spark.
4813·9	I	2	Hemsalech ‡.
4910·325	I	3	Aretz: Spark.

* *Zeit. für wiss. Phot.* xiii. p. 399 (1914).
† Dissertation (Bonn, 1911).
‡ 'Spectres d'Etincelles' (Paris, 1901).

Notes on Table III. (Copper).

(*a*) λ 3539·1 is very feeble in all the photographs and it is not possible to say definitely whether it belongs to Class I. or to Class II.

(*b*) λ 3597·8 (not previously recorded) and (*d*) λ 3764·75 are both displaced to the red by 1 Å.U. at the beginning of the arc flash.

(*c*) λ 3654·3 is displaced to the red at the making of the arc, actually coinciding with the line λ 3655·84.

both classes occurring in the interrupted arc spectra of silver, gold, and copper respectively in the region λ 5220 to λ 3380 when the initial current was 5 amperes and 350 volts were across the poles at contact (the lower pole being negative). In recording the intensities of the lines, the scale adopted ranged from 0 to 10, the former representing the weakest and the latter the strongest lines in the spectra. The intensities given for the lines of Class I are those at the beginning of the arc flash.

As pointed out by Hemsalech and the Comte de Gramont* in the interpretation of the results of their experiments with the interrupted arc, one of the many possible effects introduced into the resulting spectra is that due to the strong electric fields set up when the upper pole is just beginning to separate from the lower. In this connexion, the behaviour of the lines λλ4081·7, 4226·55 (silver), and λλ4015·8, 4056·7 (copper) under the interrupted arc conditions is interesting. These four lines occur only at the beginning of an arc flash, which would be expected since, according to Takamine †, they occur only in a strong electric field.

It may be noted here that a classification of spectral lines similar to that above was found by Milner ‡ during the course of an examination of the streamers in the electric spark. In view of the "high tension" conditions which must exist between the poles of the arc during the early stages of the flash, it seems likely that the pole lines of the present work are closely allied to the "condensed-spark" lines of Milner's classification.

"New" lines occurring in the interrupted arc spectra.

The following pole lines (Table IV.) appearing in the interrupted arc spectra of silver, gold, and copper have not been identified in the lists of arc and spark lines given by previous observers. The roman numerals refer to the classification of pole lines already described.

Catalan § gives a list of 98 new lines in the arc spectrum of silver in the region λ 4500 to λ 2300. He also gives a comparison table which shows that, with 10 exceptions, these "new" lines have wave-lengths which agree very closely with lines given by Eder and Valenta as occurring in the spark.

* *Loc. cit.* p. 306 and p. 848.

† *Loc. cit.* p. 30.

‡ Proc. Roy. Soc. A, lxxxi. p. 299 (1908).

§ "Nuevas Lineas en el Espectro de Arco de la Plata entre 4500 y 2300 U.A." M. A. Catalan, *An. de la Soc. de Fis. y Quim.* xv. p. 483 (1917).

TABLE IV.

SILVER.			GOLD.			COPPER.		
Wave-length in I.A.		Intensity.	Wave-length in I.A.		Intensity.	Wave-length in I.A.		Intensity.
3560·5	I	2	3968·7	I	5	3539·1	II?	0
3576·2	II	1	3994·1	II	2	3595·3	II	1
3630·6	II	1	4027·3	II	1	3597·8	II	2
3728·2	I	2	4171·9	II	2			
3829·3	I	1	4227·3	I	1			
3945·6	II	1	4229·2	I	1			
4012·3	II	1	4260·5	I	2			
4063·6	I	1	4361·2	II	2			
4141·6	II	1	4467·3	II	1			
4182·1	II	1	4597·2	II	1			
4281·2	II	1	4599·4	I	1			
4298·1	I	1						
4381·4	II	1						
4455·4	I	1						
4548·9	I	1						
4550·4	I	1						
4610·6	I	1						
4614·5	II	1						
4650·3	I	1						
4657·2	I	1						
4680·4	I	1						
4721·1	I	1						
4785·5	II	1						
4811·3	I	3						
4843·3	I	1						
4870·2	I	3						
4934·3	II	1						

Unfortunately, only the region λ4500 to λ3380 of Catalan's work is included in that of the present investigation. However, all the lines within this region which Catalan was able to identify with spark lines are developed in the interrupted arc spectrum of silver, most of them passing through all the stages of the arc flash.

Of the 10 lines mentioned above which Catalan failed to identify, 9 fall within the region of the present work, but none of them appear in the interrupted arc spectrum. It is important to note that Catalan's list of new lines in the arc spectrum of silver does not include any of the unidentified pole lines occurring in the spectrum of the interrupted arc between silver poles.

Duffield *, in his study of the effect of pressure on the arc spectrum of *gold*, found a large number of lines not

* Phil. Trans. A, ccxi. p. 51 (1911).

chronicled by Kayser and Runge. However, there is no agreement between the above unidentified pole lines and the lines given in Duffield's list for gold except possibly in the case of λ 4467·3 (II). This may be the line λ 4466·25 which Duffield failed to identify.

In the spectrum of the steadily-burning *silver* arc under pressures of at least 20 atmospheres, Duffield * records that the ordinary line spectrum was replaced by a number of bands. It is possible that of these bands, those at λ 4062·9 and λ 4298·0 (at 25 atmospheres pressure) have some connexion with the unidentified pole lines λ 4063·6 (I) and λ 4298·1 (I).

The unidentified copper pole lines occurring in the present work fall outside the region of Duffield's research.

Explanation of Plate.

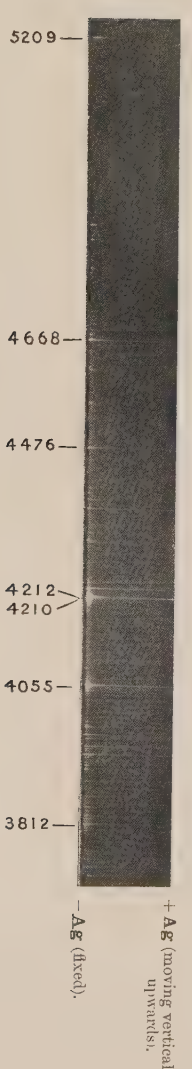
The photograph is reproduced from one of the negatives obtained when arc flashes were made between silver poles in oxygen at 350 volts and initial current 2½ amperes, the lower pole being negative. Although the distinction between the two classes of pole lines is not readily brought out, the photograph illustrates the general appearance of the pole lines and shows how they are associated with the lower fixed pole.

It will be noticed that many of the spectral lines are widened in the immediate vicinity of the lower pole. The widening is particularly noticeable in the lines λλ 4055, 4210, and is probably a manifestation of the Stark effect †. Throughout the experiments it was frequently noticed that when the widening was most evident, the pole lines were developed with the greatest intensity.

The line λ 4055 differs from all the other widened silver lines in that it is accompanied by a component on the violet side during the early stages of the arc flash. With comparatively short photographic exposures, this component is of sufficient intensity to be plainly visible in the presence of the wing on the same side of the line. The component is at its maximum distance (about 2 Å.U.) from the principal line when the upper pole just commences to leave the lower, and the distance between the two lines decreases gradually until the component finally meets the principal line when the poles are ½ to 1 mm. apart according to the voltage employed.

* *Loc. cit.* p. 43.

† Hemsalech and the Comte de Gramont, *loc. cit.*



Spectrum of Interrupted Arc between Silver Poles.

Summary.

1. Results are given of spectroscopic observations of the silver, gold, and copper arcs produced under conditions similar to those of Hemsalech and the Comte de Gramont.

2. In the region studied, λ 5220 to λ 3380, a number of lines have been found in the neighbourhood of the fixed pole which readily fall into two classes according as they cease abruptly at the end of the initial stages of the arc flash or tend to pass on into the intermediate and final stages.

3. Most of the lines have been identified with previously observed arc and spark lines, but a number of them do not seem to have been previously recorded.

4. Lists of the "new" lines occurring in the region λ 5220 to λ 3380 of the spectra of the interrupted arcs between silver, gold, and copper poles are given.

In conclusion, I desire to express my thanks to Dr. G. A. Hemsalech for suggesting the original research, for his assistance in mounting the apparatus, and for his helpful advice and criticism while the experiments were in progress. My thanks are also due to Professor W. L. Bragg, M.A., F.R.S., who has given me every facility for carrying out the investigation and has shown much interest in the development of the results.

Physics Dept.,
The University of Manchester,
July 1924.

CX. *Notices respecting New Books.*

Relativity for Physics Students. By Prof. G. B. Jeffery. Methuen. 6*s.* net.

Of the torrent of books on relativity, written for audiences of many types, from the man in the street to the scientific specialist, we would certainly select the present volume as being in some ways novel and valuable. The author has directed his attention to the growing body of young physicists who have neither the time nor the inclination to become really expert mathematicians, but who prefer to pursue their studies of physics while preserving mathematics as a useful key to unlock doors when they are found to be shut. He has succeeded in a notable way, in giving a most readable and logical account of all the essentials of the theory, without the usual excursions into the labyrinths of tensor-geometry. In fact, hardly any formulæ appear at all.

The subject-matter orginally constituted a set of University lectures intended not for the specialist, and it is perhaps a pity that the collection of a group of such lectures in this manner is not a more common event.

We can cordially recommend the book to any scientific library. It should be peculiarly adapted to stimulating the young student to pursue the subject in the more extended treatises.

The Mechanical Properties of Fluids. Blackie & Son. (Applied Physics Series.) 20*s.* net.

This is a joint work by nine authors, all of whom are experts in their respective subjects. It is, in some respects, a new departure which might well be followed in regard to other outstanding departments of Physics in which the literature at present is so deficient. It is perhaps difficult to secure the cooperation of a group of authors who are ploughing, in different directions, the broad acres of a subject closely related to some of the most fundamental things in direct technical practice. This volume at least is a brilliant success in this direction, and should prepare the way for others. It owes its inspiration to Admiral Sir George Goodwin, who is to be congratulated on the band of collaborators he has collected. It is intended primarily for engineers, but there are few mathematicians and physicists, however familiar with the current text-books on hydrodynamics, who could not learn much from its pages.

The account given of the most modern works which, as is well known, has tended so much to remove the reproach from ordinary theory of fluids that it has little relation to the behaviour of an actual fluid, is entirely up to date, and in fact written by the experts, such as Prof. Taylor, who are really responsible for the most significant advances.

The book is so arranged, and the amount of space devoted to each important aspect is so adjusted, that it can really serve as a text-book on hydrodynamics. Prof. Lamb's contribution especially bridges many gaps which would otherwise occur between the other articles.

The many subjects dealt with, apart from the general article of 45 pages on the mathematical theory of the motion of a perfect fluid, include such widely different things as viscosity and lubrication, the theory of gases, steamline flow and eddies, resistance of fluids to moving bodies, phenomena of fluid elasticity and the determination of stresses by the use of soap films, wind structure, and the practical applications of the properties of fluids involved in submarine signalling and the movement of projectiles.

The work is entirely to be recommended, and, it may well be hoped, is the forerunner of others of its class. It is an indispensable addition to any scientific library.

Hydrodynamics. By Prof. Horace Lamb. (Fifth Edition.) Cambridge University Press. 45*s.* net.

This has for so long been the classical account of this subject that the appearance of a much enlarged fifth edition is no surprise. It would, indeed, be difficult at the present day to find a writer on any mathematical topic with the peculiar clearness and lucidity displayed in all the author's writings. A great amount of the work described was done, in the first place, by himself. Yet it is difficult for one not familiar with it to distinguish it in any way from that due to others, to which Prof. Lamb lends a lucidity and charm of expression only too frequently absent from the original accounts.

All serious students of the subject will already be sufficiently familiar with earlier editions. Work in a subject regarded, not many years ago, as 'dead,' has received the most extraordinary impetus in recent years, and it is now common to hear of 'real' hydrodynamics as against the classical theory,—a rebuke to the latter which is not often expressed with complete fairness. The reader of this edition will find both, and the manner in which the author has succeeded in incorporating the recent advances into what was already a very finished treatise, without producing, at any point, a sense of discontinuity in the mind of the reader, is a notable literary achievement.

The general form of the work is perhaps the final illustration of the excellence of the mathematical series of the Cambridge University Press. In a way difficult to define, and due at least in part to the author's judicious interpolations of prose and of formulæ, this volume is more pleasant to the eye than almost all the others in the series.

X-Rays and Crystal Structure. By Sir William Bragg and Prof. W. L. Bragg. G. Bell and Sons. 21*s.* net. (New Edition, revised and enlarged.)

Such a work as this, needing a fourth edition so very soon after the third, and with the first only dating back nine years, clearly has a popularity and value which make a notice almost unnecessary. The alterations and additions which have been made alone call for detailed attention.

More exhaustive treatises have appeared recently, notably those of Dauvillier and Ewald, but the authors do not claim to be exhaustive. They, as authors of the first connected account of a new subject owing so much to their own work, are only seeking to preserve a connected account in such a manner that the influence of the most recent researches in a rapidly-developing subject shall be justly felt by the reader. It is very largely re-written and seems quite to supersede the older editions. Its scope is designed to be limited to the giving, to students of very diverse sciences, from mineralogy to physics, of a connected statement of the

present position of the subject and the methods by which it has been reached. The authors apologise for the somewhat fluid state of the terminology of the subject, which, whenever it seems fixed, is continually disturbed by a new piece of research,—and they instance Prof. Compton's work which no longer allows us to say that scattered radiation has the same wave-length as the original.

The work is full of excellent and really instructive diagrams, and its general aspect is very pleasing. We can only express the hope that further editions will be called for in the same limited periods.

The Evolution of Mathematical Physics, being the Rouse Ball Lecture of 1924. By Horace Lamb, Sc.D., F.R.S., Fellow of Trinity College, Cambridge. (Cambridge, at the University Press.)

It is certainly a most fitting and happy choice which has made Professor Lamb the Rouse Ball Lecturer for 1924. After a long and strenuous teaching career which has revolutionized the teaching of Mathematical Physics and an equally strenuous life of Research which has marked out and illumined large territories in mathematical physics, Professor Lamb has returned to Cambridge, and any opportunity of hearing him is to be seized upon. In the course of this lecture, which we are very glad to have in print, a rapid survey is taken of the currents of mathematical physics, as developed by the great writers of the eighteenth and early nineteenth century. The starting point of mathematical physics is fixed by the publication of Poisson's first memoir on Sound in 1807—a year which is also memorable for the first instalment of Fourier's investigations on the Conduction of Heat, whose importance extends far beyond the special subject *a propos* of which the trigonometric series for ever to be associated with his name arose. The great flow of production from this time onwards is associated with a group of famous names: Oersted's discovery of the action of an electric current on a magnetic needle came in 1820; Ampère's work on the mechanical action between electric circuits followed soon after. The researches of Navier, Cauchy, and Poisson on Electricity were followed by Green's Essay on Electricity and Magnetism in 1828. Neumann, twenty years later, developed further the ideas of Ampère. Professor Lamb continues the thrilling story of nineteenth century mathematics and mathematicians, touching in turn on the work of Kirchhoff in Electric Induction, of Stokes in Diffraction, of Helmholtz in Vortex Motion, and on the remarkable work of Maxwell in many domains.

We can heartily recommend this lecture to the attention of mathematicians and physicists. It teaches the great lesson which was better known to the last generation than to the present generation, that "l'étude approfondie de la nature est la source la plus féconde des découvertes mathématiques."

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. By Dr. J. W. Mellor. Vol. 5. (Longmans, Green & Co. 63*s.* net.)

The fifth volume of this enormous undertaking is devoted to the elements Boron, Aluminium, Gallium, Indium, Thallium, Scandium, Cerium, and the rare earth metals to a smaller extent. To the treatment of the rare earths, a sequel is to follow.

The work proceeds on the same comprehensive lines as before. The only possible criticism is that it is by far too comprehensive—not in the sense of dealing with all known qualitative or quantitative phenomena relating to these elements, but in the sense that it includes too much literature. The feeling we had about earlier volumes is intensified by the study of this one,—that the discrimination between good and bad work among such a multitude of authors has not been carried out effectively. In fact, the author does not appear, in his plan, to include such an attempt. Consequently a student, turning to these pages for help in a given matter, may be overwhelmed by the wealth of references he will find, and the absence of any guidance to him as to which he should read and which he may ignore, at least in the first instance. The relative value of various views of any given topic might well be stated also in many instances.

But as a final work of reference, or as a dictionary of chemical literature and knowledge, the work is quite unrivalled. It has appeared very soon after the preceding volume, and it is perhaps hardly fair to expect an author, who has had the great courage required for an undertaking of this magnitude, and the untiring industry apparent in every page, to be able to go further on the lines we have mentioned.

There is at least no doubt that the presence of this series in a library will save it great expense, in the long run, on miscellaneous periodical literature, and will be of extreme value to readers.

Alternating Current Rectification. By L. B. W. Jolley. (Chapman and Hall. 25*s.* net.)

This is a very welcome book. The author is one of the research staff of the General Electric Company, with necessarily a large experience of actual rectifiers of many designs. In a very new subject such as this, with the enormous developments recently due to, for example, the introduction of the thermionic valve, it has been impossible for the new editions of ordinary works on electricity or even its technical engineering side to keep pace with progress.

This work completely fills the gap on the practical side as it now exists, though it would be difficult to say how rapidly the gap may continue to widen again. A very welcome feature is the use which the author has made of the patent literature, which, as a rule, requires a long time before it really influences text-books.

There is an abundance of useful diagrams of the apparatus described, and the work is pleasant to read, and very free from misprints. It will form a useful addition to the library of any electrical engineer, or certain types of specialist in electrical physics.

Modern Astrophysics. By Prof. H. Dingle. (Collins, Sons & Co. Ltd. 30*s.* net.)

We have long needed a comprehensive account of astrophysics, inclusive of all the newer views in a science which advances more rapidly today than almost all others, and has already ceased to be in any way a subsection of astronomy or of physics. An author of such a work has a great opportunity of giving a balanced survey of a subject in which, at every hand, it is possible to hold very different opinions and quote equally weighty experts on either hand.

We fear that the author has not seized this opportunity. The work is a mine of information which is only otherwise to be obtained by laborious search among scientific journals, and on this account alone it is of great value to a reader who wishes to learn the nature of the phenomena and some of the theories which have been proposed towards their elucidation. On the practical side, in fact, the work is not readily reproached. The account of the phenomena and of modes of investigation is excellent throughout, though written at times in a manner which vaguely suggests the theatre—the author is far too fond of filling the middles of his paragraphs with notes of interrogation.

In so far as he is clearly the type of worker who is not prepared to believe any thing which eyes have not seen in a laboratory, he is at least consistent, and a reviewer would not quarrel with his treatment. But this fact hardly justifies him in the implicit assumption that there is no phenomenon shown, for instance, by the spectra of celestial bodies, which cannot ultimately be reproduced in the limited space of a vacuum-tube. Nor is it appropriate to dismiss, as he does in several instances, investigations of a theoretical nature which are now, or have been, important, with the briefest of mention on the sole ground that the laboratory has given, as yet, no evidence for or against them. They should at least be effectively presented for the reader to have a chance to formulate his own view as to their merits.

The writer is clearly not a mathematician, but it is not investigations of this class alone to which we refer. He has, in fact, not given a really critical survey, but rather that of an advocate,—and not always a consistent one. But in spite of what must be regarded as defects, which may be remedied in future editions which are likely to be called for, we nevertheless would congratulate the author on a very difficult piece of compilation and on the production of what is, in effect, our first book dealing in a general way with the whole range of astrophysics. In the final chapter, on "astrophysics as it will be," the author, as sometimes in earlier sections, is somewhat carried away by his own language, and ceases to be quite scientific.

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